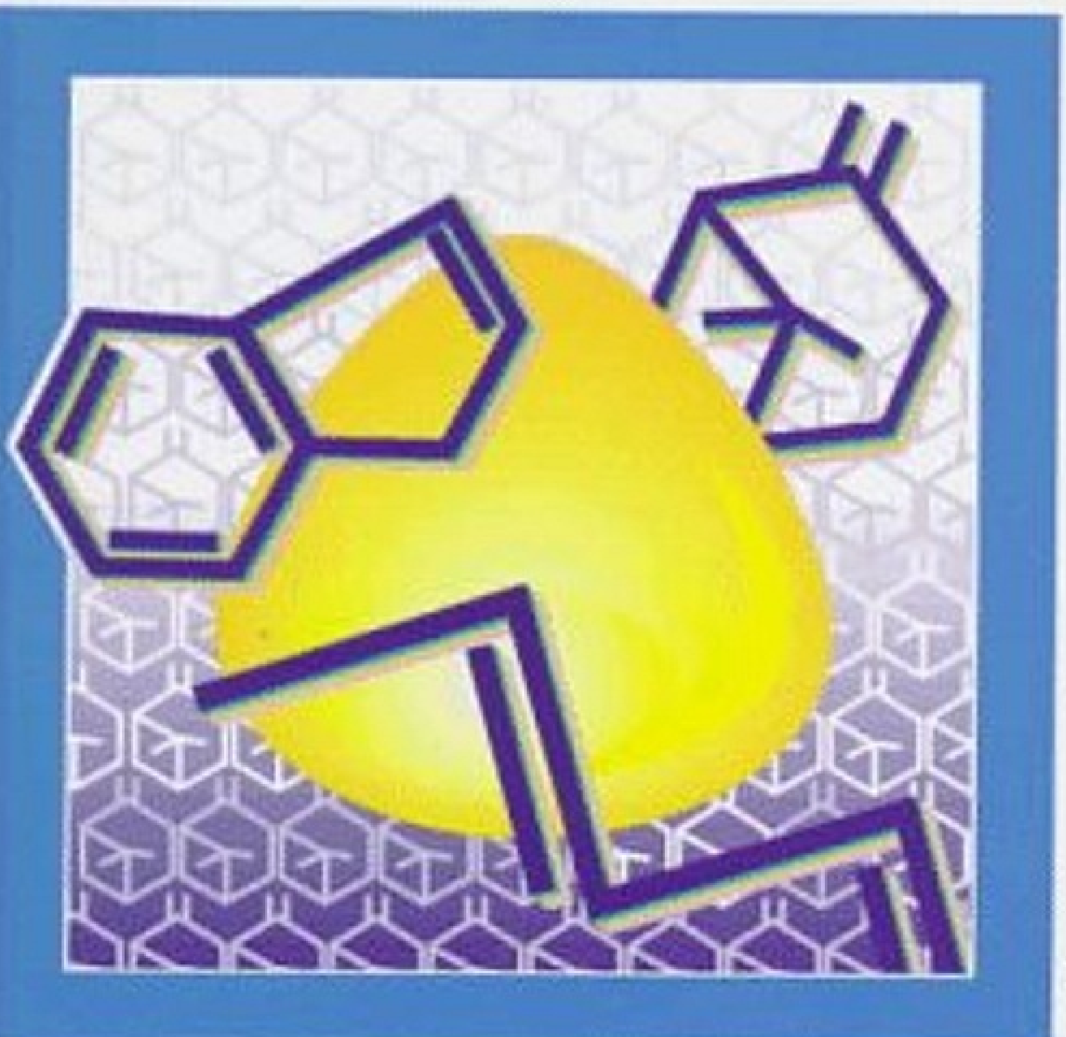
R. Mildenberg
M. Zander
G. Collin

Hydrocarbon Resins



VCH
A Wiley company

R. Mildenberg, M. Zander, G. Collin

Hydrocarbon Resins

VCH
A Wiley company

R. Mildenberg, M. Zander, G. Collin

Hydrocarbon Resins

VCH
A Wiley company

Dr. Rolf Mildenberg
Gaußstraße 7
D-45468 Mülheim an der Ruhr

Dr. Gerd Collin
DECHEMA e.V.
Theodor-Heuss-Allee 25
D-60486 Frankfurt a. M.

Dr. Mechthild Zander
8, Impasse Kreuzheck
F-57350 Spicheren

Published jointly by
VCH Verlagsgesellschaft mbH, Weinheim (Federal Republic of Germany)
VCH Publishers. Inc., New York, NY (USA)

Editorial Director: Dr. Barbara Böck
Production Manager: Peter J. Biel
Cover Illustration: Susanne Baum

Library of Congress Card No. applied for
A CIP catalogue record for this book is available from the British Library

Die Deutsche Bibliothek – CIP-Einheitsaufnahme
Mildenberg, Rolf:
Hydrocarbon resins / R. Mildenberg ; M. Zander ; G. Collin. –
Weinheim ; New York ; Basel ; Cambridge ; Tokyo : VCH, 1997
ISBN 3-527-28617-9
NE: Zander, Mechthild:; Collin Gerd:

Printed on acid-free and low-chlorine paper

Composition: Graph. Werkstätten Lehne GmbH, D-41516 Grevenbroich
Printing and Bookbinding: Strauss Offsetdruck GmbH, D-69509 Mörlenbach

Printed in the Federal Republic of Germany

Acknowledgement

The authors are particularly grateful to VCH Verlagsgesellschaft mbH, Weinheim (Germany) for suggesting the project, and for the design and production of this book.

Furthermore, they are greatly indebted to Dr. Barbara Böck for her work in supervising the project, and to Dr. Don Emerson for proofreading, which has contributed to minimizing errors.

The authors would also like to express their gratitude to the members of the Technical Service Dept. of VFT AG/Rütgerswerke, Duisburg (Germany) for the support given. Special thanks are due to Mr. Wolfgang Lücke, VFT AG, for preparing the flow sheets.

The authors would like to acknowledge the helpful contribution by constructive criticism of Dr. Emile Yax, formerly responsible for resin R & D of CdF Chimie (France), and of Mr. Allan Dury, Altovar Ltd., Banbury, Oxon (UK).

Grateful acknowledgement is made of the valuable support rendered by Cray Valley, Paris, Elf Atochem, Paris, Nevcin Polymers B.V., Uithoorn (Holland), and Shell Chemicals Europe Ltd., London (UK) for authorization of publication.

Preface

With the ever-increasing requirements of the market, the demand for better quality control, constant products, and other aspects, chemists, engineers, and applications technologists are no longer satisfied with mere knowledge of the physical data of the chemical base products they employ. They are increasingly interested in the raw materials used, in production techniques, and specific physical and chemical characteristics with regard to their applications. Therefore, general technical data of resins are not the only factors to be considered when selecting an appropriate resin type for a specific end use.

Most of the hydrocarbon resins on the market are not manufactured from a simple, well-defined, pure monomer, but from more or less complex monomer mixtures. They are mixtures of a number of polymerizable constituents, often with quite different polymerization behavior. Each component contributes to the characteristics of the different resins, or to be more precise, of the resin blends. Characteristics of the resulting resin can often be traced back to the source and chemical composition of the starting materials, i.e., to their fundamental chemical nature.

On the other hand, the manufacturing technique may also contribute significantly to the resin's character, for instance, the molecular mass distribution and hence the solubility.

However, without doubt, it is the chemical composition which has the most decisive influence on resin properties. The composition and chemical characteristics of the individual resin components have a great, if not decisive influence on their suitability in specific areas of application, and on their properties and performance.

For these reasons, the authors have endeavoured to point out how each phase of the resin manufacturing process, from raw material to end product, as well as the chemical composition influence their applications and properties.

The present publication is mainly based on the authors personnel experience and knowledge.

This book is not meant to be a comprehensive manual of hydrocarbon resins; it aims to provide chemists, process engineers, applications technologists, technical sales personnel, and students of chemistry and chemical engineering, with a concise, overall view of raw materials, manufacture, physical and chemical properties, and the manifold applications offered by the various commercially available hydrocarbon resins.

A systematic bibliographic research has not been considered useful.

Contents

1 Terminology

The term "resin" is not sharply defined; originally, it was applied to low molecular mass natural products, usually yellowish to brown in color, transparent to opaque, soft to brittle, easily fusible, tacky, amorphous materials, soluble in most common organic solvents and virtually insoluble in water. With the development of chemical industry, the term resin has also been applied to synthetic materials used as substitutes for natural resins, or to materials with similar physical properties. In the international standards ISO 472 (Plastics-Vocabulary) and ISO 4618/3 (Paints and Varnishes, Part 3: Terminology of Resins), resins are defined as solid, semisolid, or pseudosolid organic materials that have an indefinite and often high relative molecular mass, and generally soften or melt over a range of temperatures. Very often the term resin is also used for any polymer that is a basic material for plastics (e.g., polyethylene resin). In the German standard DIN 55958, resin ("Harz") is used as a collective term for solid to liquid organic products. Their molecular mass distribution can vary over a wide range. Resins include a variety of organic substances of different chemical composition, but with many physical properties in common.

Generally, resins are products with medium molecular mass. Their average molecular mass does not usually exceed 10 000 and, in most cases, is much lower. Resins have an amorphous and often complex structure. They do not exhibit a sharp melting point, but like all amorphous polymer systems, have a glass transition temperature, and are characterized by their softening point – the transition temperature from a pseudosolid to a plastic state.

Resins can be subdivided into natural and synthetic resins.

1.1 Natural Resins

In ISO 4618/3, natural resins are defined as resins of vegetable or animal origin. The term includes rosins, i.e., gum, wood, or tall oil rosins from tree and plant exudates, wood extracts or by-products of paper manufacturing; fossil resins such as amber; mined resins such as asphaltite; secretion products from insects such as shellac; and their main derivatives.

1.2 Synthetic Resins

In ISO 4618/3, synthetic resins are defined as resins resulting from controlled chemical reactions, such as polyaddition or polycondensation between well-defined reactants, that do not themselves have the characteristics of resins. Synthetic resins are also obtained by polymerization (ISO 472) of unsaturated monomers. This term includes two subgroups:

- Hydrocarbon resins, i.e., synthetic resins from coal tar, petroleum, and turpentine feedstocks, produced by polymerization. These resins are used like natural ones, e.g., in combination with other polymers to impart special properties, such as tack, flow, and hardness, to a material.
- Synthetic resins, obtained mainly by addition polymerization and polycondensation, which are intermediates in the synthesis of higher molecular mass plastics.

Resins may be further classified:

- by origin: natural or synthetic resins; petroleum, terpene, or coal-tar resins (indene-coumarone resins or coal-tar pitch)
- by physical aspect: liquid, soft or hard resins
- by the reaction mechanism of their production or processing: resins from polyaddition, polymerization, or polycondensation
- by application and processing: resins for paints and varnishes or printing inks; tackifying, casting, laminating, or impregnating resins
- by other characteristics: thermosetting, thermoplastic, saponifiable resins, etc.
- by intended modification of product properties: tackifier, plasticizer, processing aid, hard resin, fixing resin, etc.

This book covers those hydrocarbon resins which are synthetic resins obtained by polymerization.

2 Raw Materials for the Manufacture of Resins

The main sources of raw materials for the production of hydrocarbon resins are pyrolysis processes, e.g., pyrolysis of coal in coke ovens to make indene-coumarone resins and, to a larger extent, pyrolysis of petroleum fractions in steam crackers to make petroleum resins. The raw material for the production of terpene resins is based on natural terpene monomers, mainly obtained from naval stores and paper production, and to a less extent from extraction of orange peel in the production of orange juice. Other valuable resin precursors are commercial monomers of the styrene type.

Since the composition of the feedstock has an important effect on the properties of the resin produced, and the presence of impurities can effect the polymerization, processing of the initial crude feedstock plays a key role in the manufacture of different resin types.

It is also important to note that, beside "straight" resins from well-defined sources such as coal tar, petroleum, terpenes, or commercial monomers, all kinds of mixed resins based on combinations of these feedstocks are produced.

2.1 Indene-Coumarone Resins

The basic material for the production of indene-coumarone (IC) resins is high-temperature coal tar, the oldest source of a multitude of aromatic starting materials for the chemical industry. Indene and coumarone were discovered by the German chemists Krämer and Spilker in 1890 [2.1]. The first IC resins were manufactured on a commercial scale in Europe in 1910.

Coal tar is one of the by-products of coal carbonization. In the well-known horizontal coking process, hard coal undergoes a pyrolytic conversion in horizontal chamber coke oven batteries at temperatures of 1000–1200°C. The main product is, of course, coke, but there are also a number of by-products, some of them liquid at normal temperatures, partly recoverable by condensation and extraction (washing) from the gaseous products liberated during carbonization. The most important products and the average respective quantities (wt%) obtained in the coking process are:

– Coke	ca. 75
– Crude tar	3
– Crude benzene	1

For economic reasons, coal tar is collected in central refineries for upgrading and distillation to recover aromatic chemicals.

The first stage in the distillation of coal tar gives water and so-called coal-tar light oil (0,5–3% of the total tar). This, and the following fraction, carbolic oil, after extraction of

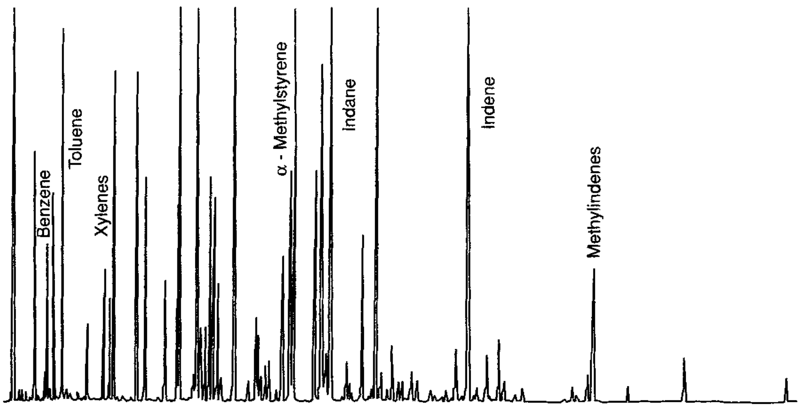


Figure 2.1 Gas-liquid chromatogram of a light oil fraction from coal tar

phenols and bases, are the major sources of the unsaturated polymerizable aromatic compounds used in the manufacture of indene-coumarone resins.

The amounts of the various primary distillation products from high-temperature coal tar are (wt%):

– Light oil	0.5– 3
– Carbolic oil	2 – 3
– Naphthalene oil	10 –12
– Wash oil	7 – 8
– Anthracene oil	22 –28
– Pitch	50 –55

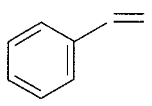
The light oil fraction boils in the range 70–200°C, has density 0.91–0.96, and contains not only benzene, toluene, and xylenes, but also 10–40 % of unsaturated aromatics, as well as 3–10 % phenols and 2–7 % pyridine bases.

Figure 2.1 shows a gas-liquid chromatogram of a typical light oil fraction.

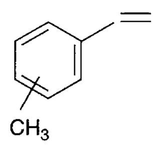
The composition of a typical indene-coumarone feedstream is (wt%):

– Styrene	2.0
– α-Methystyrene	1.0
– Alkylbenzenes	30.0
– Vinyltoluenes	4.0
– Dicyclopentadiene	5.0
– Coumarone	7.0
– Indene	48.0
– Methylindenes and methylcoumarones	3.0

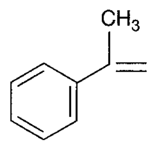
The structures of resin formers in coal-tar light oil are:



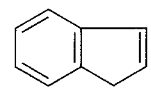
Styrene



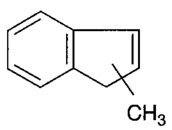
Vinyltoluenes



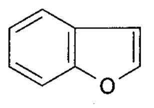
α-Methylstyrene



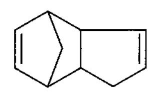
Indene



Methylindenes



Coumarone



Dicyclopentadiene

A GLC scan of an indene-coumarone resin feedstock is shown in Figure 2.2.

Additional unsaturated higher boiling hydrocarbons, mainly indene and methylindenes, may be recovered from carbolic and naphthalene oil after separation of naphthalene by crystallization and fractionation of the filtrates (secondary light oil).

The boiling points (°C) of recovered unsaturates are:

– Styrene	145.1
– 2-Vinyltoluene	169.8
– Dicyclopentadiene	170.0
– Coumarone	171.4
– α-Methylstyrene	172/173
– Indene	182.4
– 7-Methylcoumarone	190/191
– 6-, 4- and 5-Methylcoumarone	192/199
– 4-Methylindene	209.0
– 4,6-Dimethylindene	212.0
– 4,5-Dimethylindene	220.0

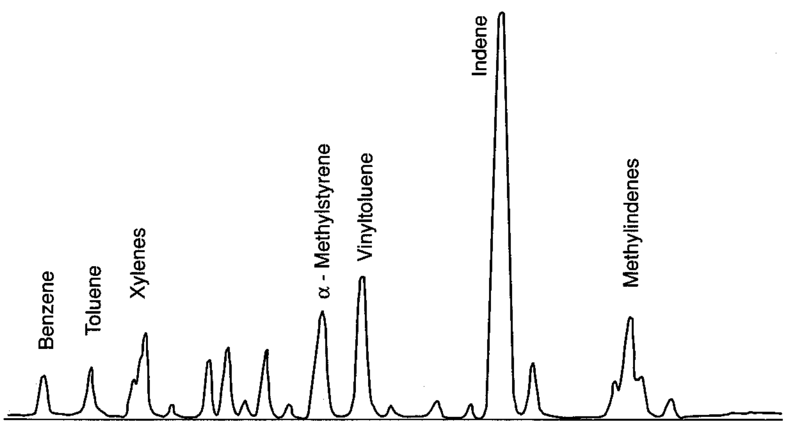


Figure 2.2 Gas-liquid chromatogram of an indene-coumarone resin feedstock (simplified)

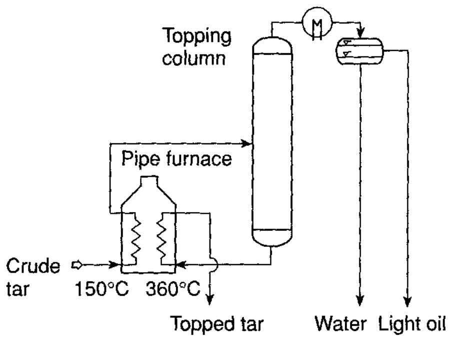


Figure 2.3 Recovery of water and light oil from coal tar

It should be noted that, in some tar refining processes, the higher boiling unsaturated compounds, recovered for instance from the carbolic and naphthalene oil fractions may have a different "thermal history" from that of the original light oil. Consequently, in certain steps of coal-tar processing, the unsaturated compounds contained in tar oils can be submitted to excessive thermal treatment. After separation of the original primary light oil, together with the water from the crude tar, the so-called topped tar flows through the high-temperature section of the pipe furnace (Figure 2.3) for further distillation steps, i.e., separation of the other tar oil fractions from the pitch residue.

During these high-temperature operations intermolecular hydrogen transfer reactions occur, transforming some indene to indane. Process improvements (lower distillation temperature and residence time) may reduce indene loss considerably. It has also to be noted, that high indane concentrations in the resin feedstocks causes serious problems in the polymerization process (lower yield, poor quality). In fact, this is not due to indane itself, but seems to be caused by unknown impurities, in very small or even trace amounts, probably substances such as benzonitrile and benzophenone.

Further processing of resin feedstocks is usually integrated in the resin manufacturing units.

Despite fluctuations in the international coke-making scene, connected with steel production, the availability of crude tar as raw material for indene–coumarone resins is sufficient to satisfy demand (ca. 16×10^6 t/y).

2.2 Raw Material for Petroleum-Based Resins

An alternative source of raw material for resin production became available with the development of the petrochemical industry in the 1940s. The pyrolysis of natural gas, ethane, propane, naphtha, kerosene, or heavier petroleum fractions provides large quantities of unsaturated compounds as by-products in the production of ethylene.

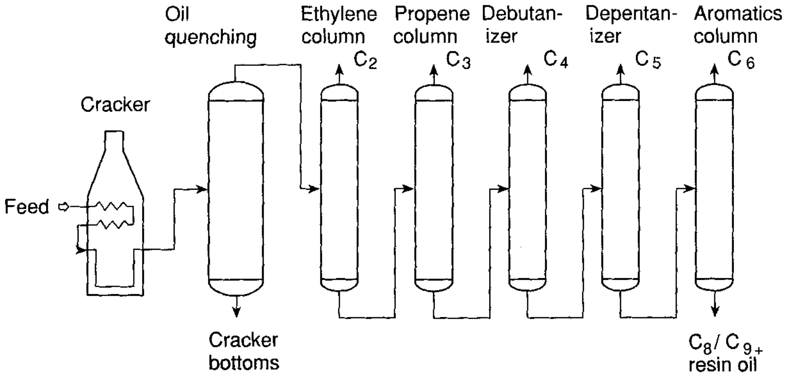


Figure 2.4 Schematic diagram of a steam cracker

The pyrolysis operation is carried out at ca. 650–900 °C at normal pressure in the presence of steam. The so-called steamcracking process (Fig. 2.4) involves radical reactions, mainly carbon–carbon bond splitting, of saturated, unsaturated, and aromatic molecules:

$$2\ H_3C - CH_2 - CH_3 \text{ (propane)} \longrightarrow \begin{cases} H_2C = CH_2 + CH_4 & \text{(ethylene, methane)} \\ CH_3 - CH = CH_2 + H_2 & \text{(propene)} \end{cases}$$

Depending on the type of the initial feedstream, full-range naphtha, light gas oil, heavy gas oil, etc., the relative proportions of the different constituents vary. The pyrolysis of naphtha fractions can generate the following products, depending on the origin of the naphtha and the cracking conditions (amounts in wt%):

– Hydrogen	1.0
– Methane-rich gas	15.0
– Ethylene	28.0
– Ethane	3.5
– Propene	14.0
– C_4 fraction	9.0
– C_5 fraction	3.0
– Benzene	7.5
– C_6 fraction	1.0
– Toluene	5.0
– C_8 Aromatics	3.0
– C_9 Aromatics	3.5
– Residual oil	5.5

As the main purpose of steamcracking is the production of ethylene and propene, the selection of cracker feedstock depends on ethylene and propene yield, price and availability.

The following steam cracker fractions are used as raw materials for petroleum resin production:

- C_5 streams, containing linear and cyclic olefins, to produce aliphatic resins
- C_8/C_9 streams, containing unsaturated aromatics, such as styrenes and indenes, to produce aromatic resins
- DCPD (dicyclopentadiene) streams, to produce dicyclopentadiene resins
- C_4 streams, containing olefins, to produce polybutene resins.

C_9

2.2.1 Aromatic Hydrocarbon Resins

Usually the downstream operations finish up at the so-called depentanizer stage. All C_5 and higher boiling components (pyrolysis benzene) are hydrogenated and finally reach the gasolin sector. Nevertheless, some petrochemical companies also operate a separate downstream aromatic column. There are only few facilities in Europe, the United States, Japan, Korea, and Taiwan that are technically equipped to offer a C_9 resin oil for resin manufacturing.

Benzene, together with toluene and xylene, is drawn off as the top product and a C_9 material is obtained as a sidestream or residue depending on the process. This material contains high-boiling benzene homologs, in particular unsaturates with a boiling range of ca. 160–200 °C. (Fig. 2.5).

Depending on column operation conditions, raw material composition may be adapted to a certain extent to the requirements of resin producers.

Most buyers of C_9 resin oils require a very low content of cyclopentadiene (and dicyclopentadiene), normally less than 5–7 %. For this reason the producers of resin oil aim for the lowest possible residence time for this downstream step to achieve a narrow temperature range and a relatively low overall temperature level in the aromatics column. A limited residence time in intermediate and storage tanks is also advisable.

C_9 resin oils with higher styrene content or oils blended with technical dicyclopentadiene material are also available.

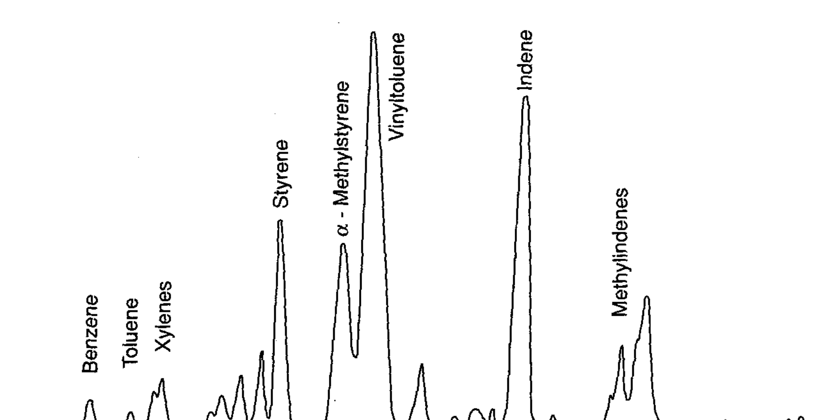


Figure 2.5 Gas-liquid chromatogram of a C_9 hydrocarbon resin feedstock

A typical C_9 resin oil has the following composition (wt%):

- Styrene	2
- α-Methylstyrene	4
- Vinyltoluene	20
- DCPD and codimers	6
- Indene	20
- Methylindenes	5
- Naphthalene	5
- Other nonreactive aromatics	38

The resin oil can be considered as a "tailor-made" fraction, used mainly in C_9 resin manufacture.

A further source of C_9 raw material is from the bottoms of oil quenching (pyrolysis oil). To a certain extent this residual oil is similar to coal tar, and contains a similar range of aromatic substances. Traditionally used as fuel or as carbon-black feedstock, this pyrolysis oil is upgraded by coal-tar processing companies. Distillation gives, among other oils, a C_9/C_{10} resin oil with a higher methylindene content.

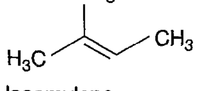
Thus, feedstreams for the production of aromatic resins come from two sources: coal tar and petroleum. Structures of resin precursors in both types of raw material are roughly identical. An exception is the presence of small quantities of coumarone in coal-tar-based feedstreams. There is a significant difference in the concentrations of individual monomers; coal-tar-based raw material is richer in indene structures, with a styrenes: indenes ratio ca. 1 : 7, whereas in petroleum-based feedstreams this ratio is ca. 1 : 1. For this reason C_9 streams offer more possibilities for flexibility in selecting wider or narrower cuts around certain constituents of this fraction. Knowledge of the composition and chemistry of resins based on C_9 streams is a great help in resin selection, which is dealt with in greater detail in Chapter 6.

2.2.2 Aliphatic C_5 Hydrocarbon Resins

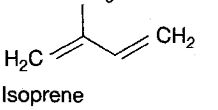
Raw material for the production of aliphatic C_5 hydrocarbon resins comes from the depentanizer effluents (Fig. 2.4). This crude C_5 fraction consists of olefins and diolefins, such as isoamylene, isoprene, piperylene, and cyclopentadiene, together with C_5 paraffins. An example of a possible composition is given in Table 2.1.

The unsaturated components of this fraction are the basis for resin production.

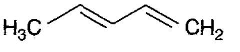
Structures of C_5 olefins and diolefins:



Isoamylene
(2-Methylbutene-2)

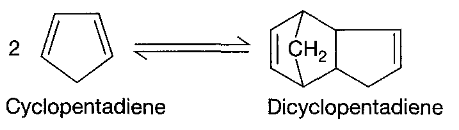


Isoprene



Piperylene
(1,3-Pentadiene)

It should be noted that cyclopentadiene, CPD (C_5), undergoes dimerization to dicyclopentadiene, DCPD (C_{10}) by a Diels-Alder reaction even at room temperature. Thus, partially left in the depentanizer bottoms, it finally ends up in the C_{9+} fraction. At higher temperatures DCPD depolymerizes back to CPD.



This crude C_5 fraction is not suitable for the production of valuable resins, owing to the presence of cyclopentadiene, which is thought to be a gel precursor. Improvements are achieved by heat-soaking to dimerize cyclopentadiene, thus reducing the concentration of this undesirable component. The DCPD concentrate (with ca. 65 % DCPD) is the basis for the production of DCPD resins (see Section 2.2.3). The heart cut is further distilled or extractively distilled to separate isoprene from the piperylene concentrate, which is the feedstock for the manufacture of C_5 resins.

Examples of possible compositions of C_5 resin feedstock are given in Table 2.1.

A well balanced diolefin/monoolefin ratio and the nature of the monoolefins present are important variables. The molecular mass distribution of the final resin, and the overall course of the polymerization process, can be affected by the types of monoolefins in the feedstock.

The ratio of isoprene/piperylene (*cis-* and *trans*-piperylene) may also vary, but it is rare to find a commercial C_5 resin feedstock without a definite isoprene content, although it is possible to produce C_5 resins on the basis of piperylene only.

An example of a gas-liquid chromatogram of a C_5 resin feedstock is shown in Figure 2.6.

Table 2.1 Typical Composition of C_5 Resin Feedstock

Raw materials	Straight, (wt%)	Distilled concentrate, (wt%)	Extractive distillation concentrate, (wt%)
Cyclo- and dicyclopentadiene	19.0	7.5	2.0
Isoprene	30.0	8.0	0.5
Piperylene	14.0	38.0	69.0
Pentenes	15.0	12.5	0.5
Pentanes	11.0	15.0	2.0
Cyclopentene	2.0	8.5	18.0
Other hydrocarbons	9.0	10.5	8.0

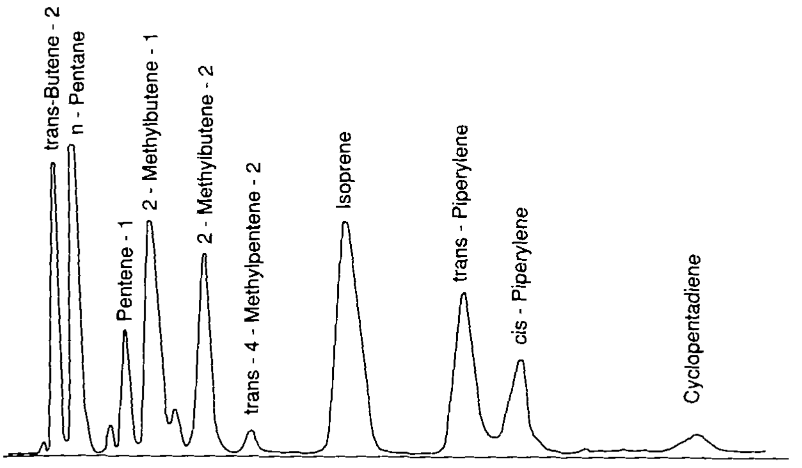


Figure 2.6 Gas-liquid chromatogram of a C_5 hydrocarbon resin feedstock (simpliefied)

For economic reasons, the availability of piperylene concentrates is closely connected with the isoprene market, as the distillation step is too expensive to be used exclusively for making resins.

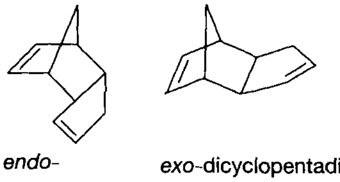
Isoprene is used mainly for the production of synthetic rubber, e.g., polyisoprene and butyl rubber, more or less in competition with natural rubber, and also for thermoplastic rubber (styrene block copolymers) as the backbone polymer in the formulation of hot-melt adhesives.

2.2.3 Dicyclopentadiene Resins

Dicyclopentadiene (DCPD) concentrates are generated in the heat-soaking process of the depentanizer effluents and subsequent fractional distillation of C_5 fractions. The concentration of DCPD may vary from high (90–95 %) through medium (70–80 %) to relatively low. Codimers with other dienes, such as butadiene or isoprene, and methylcyclopentadiene may also be present. A specification of a typical DCPD raw material is given in Table 2.2.

A GLC scan of a CPD/DCPD resin feedstock is shown in Figure 2.7.

Dicyclopentadiene exists as two stereoisomers, the *endo-* and *exo-*isomer. At 20 °C the endo form is predominant.



endo- *exo*-dicyclopentadiene

Table 2.2 Specification of a typical DCPD concentrate

Composition		Properties	
DCPD	65–98 wt%	Color	≤ 20 Hazen
Codimers	2–35 wt%	Density	0.94–0.98 g/cm^3
Polymerizables	≥ 96 wt%	Boiling range	145–180 °C
Benzene	≤ 1 wt%	Flash point	ca. 21 °C
Sulfur	≤ 150 ppm		

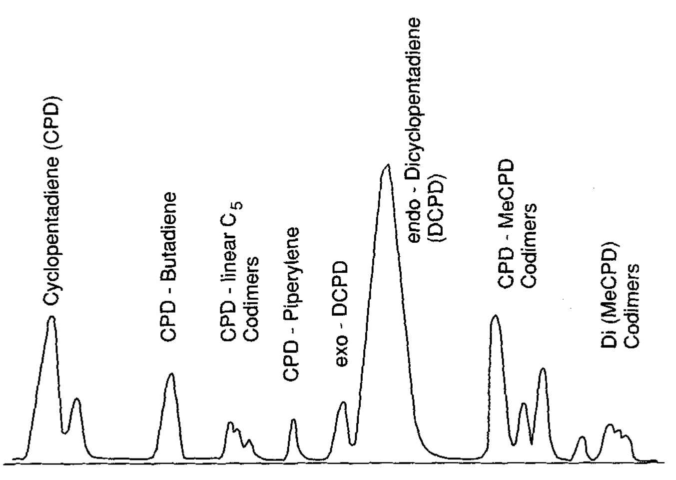


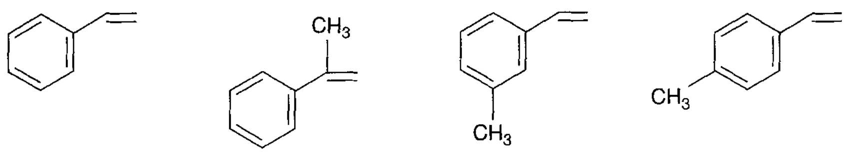
Figure 2.7 Gas-liquid chromatogram of a CPD/DCPD resin feedstock (simplified)

The contents of DCPD and codimers, as well as the total of unsaturated polymerizable components, are important for the yield and the characteristics of the product. The sulfur content decides the final resin's suitability for any subsequent hydrogenation process that may be envisaged; too high a peroxide content, and the initial color of the DCPD feedstock have a strong influence on the color level of the resulting resins.

2.3 Resins from Pure Commercial Monomers

In contrast to petroleum and coal-tar-based resins which are produced from more or less impure mixtures, there are also resins available, which are essentially colorless, made from pure unsaturated monomers, such as styrene, α-methylstyrene, and vinyltoluenes.

These monomers are used individually or as blends, sometimes together with terpenes or other selected unsaturated aliphatics to obtain high-grade resins with specific properties.



Styrene α-Methylstyrene   *m*-Vinyltoluene   *p*-Vinyltoluene

Styrene is produced in large quantities, mainly for production of polystyrene, by alkylation of benzene with ethylene in the presence of catalysts such as aluminum chloride, and subsequent dehydrogenation.

Commercial α-methylstyrene is a valuable by-product in the large-scale production of synthetic phenol by oxidation of cumene to the hydroperoxide and subsequent splitting by acids.

Vinyltoluenes are manufactured by only a few producers using the alkylation of toluene and subsequent dehydrogenation. Alkylation produces an isomeric mixture of *o*-, *m*-, and *p*-ethyltoluene. As *o*-ethyltoluene may undergo cyclization, it is eliminated before dehydrogenation. After distillation, the mixture contains 64.5 % *m*- and 35.5 % *p*-vinyltoluene. More recently the pure *p*-isomer has become available.

2.4 Polyterpene Resins

The feedstocks for the production of terpene resins are natural terpene monomers, obtained from naval stores, paper pulp production, and citrus juice production. Terpenes are found in nearly all living plants; turpentine oil from pine trees is the most important natural source. It is available as gum, wood, and tall-oil turpentine.

Gum turpentine is obtained from wounding living trees to get an exudate containing rosin and turpentine. Turpentine is separated from the rosin by continuous steam distillation and further fractionation. Wood turpentine comes from the extraction of stumps of pine trees by naphtha, and subsequent separation of rosin and turpentine by fractional distillation. Tall-oil turpentine is a by-product of Kraft sulfate paper manufacture. Terpenes are isolated from the sulfate turpentine and separated from the black digestion liquor.

The composition of turpentine oil depends to a large extent on its source, as shown in Table 2.3.

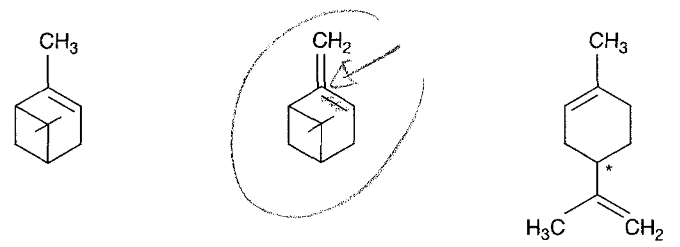
Table 2.3 Composition of turpentine oils

	Gum turpentine, wt%	wood turpentine, wt%	tall-oil turpentine, wt%
α-Pinene	58–65	ca. 80	60–70
β-Pinene	23–35	0– 2	20–25
Camphene		4– 8	
Other terpenes	5– 8	15–20	6–12

A well-known use for turpentine oil is as a solvent in the paint and lacquer industry. Crude turpentine is converted to a number of refined products by sophisticated fractional distillation used in the fragrance and flavor industry.

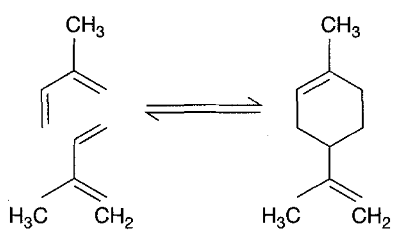
D-Limonene is obtained from citrus fruits, mostly by extraction from orange peel, which are by-products in the production of orange juice.

Of the three groups of terpenes, acyclic, monocyclic, and bicyclic, only the unsaturated mono- and bicyclic terpenes are of interest for resin production. These are mainly α-pinene, β-pinene, and dipentene (D,L-limonene).



α-Pinene β-Pinene Dipentene (Limonene)

Chemically, terpenes may be classified as isoprene derivatives. Dipentene can be synthezised by Diels-Alder dimerization of isoprene



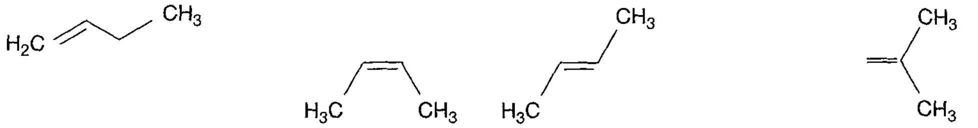
2.5 Polybutene Oligomers

Low molecular mass polybutenes are usually produced from C_4 refinery streams derived from steam cracking of petroleum fractions.

These C_4 fractions contain valuable olefins, mainly isobutenes, suitable for producing polybutene oligomers by cationic polymerization. After removal of butadiene, a feed-stream may be obtained with the following approximate composition (wt %):

- 1-Butene	ca. 10
- *cis*- and *trans*-Butene	10–15
- Isobutene	15–30 or more
- *n*-Butane	ca. 30
- Isobutane	ca. 30
- C_5 and higher components	balance

Structures of C_4 unsaturated components:



1-Butene

cis- *trans-*
2-Butene

Isobutene

As purification and separation of the isomers is relatively expensive, polybutenes are usually produced from the above mixtures with isobutene as the major component. Smaller quantities of oligomers are also produced from pure monomers.

3 Resin Manufacture

Manufacture of hydrocarbon resins involves the following main steps:

- Selection and pretreatment of raw material
- Polymerization of the prepared feed
- Deactivation of initiating system (neutralization)
- Separation of resin

The raw material for the production of hydrocarbon resins is mainly a multicomponent mixture, containing the resin formers together with nonpolymerizable material and impurities of variable concentration. All these constituents may affect both, the polymerization reaction and the properties of the resin. Therefore, careful treatment of the raw material is of the utmost importance.

Processing of raw material may include various techniques:

- Washing processes to eliminate impurities, e.g., phenols and nitrogen bases
- Preheating to eliminate undesirable heat-reactive constituents
- Prepolymerization to remove highly reactive undesirable components
- Distillation to remove light and heavy products and to adjust the composition and concentration of resin formers

The resin forming step consists in oligomerization of unsaturated reactive constituents by contacting the feed with an appropriate initiating system. The reaction is a carbocationic polymerization, yielding low to moderately high molecular mass products, ranging from $\overline{M}_n$ ca. 500 to $\overline{M}_n \geqslant 1000$.

There is not much scientific information available on industrial processes employing carbocationic polymerization; companies tend to regard technical details as industrial secrets.

It is obvious that the phenomena in complicated mixtures such as feedstreams, containing resin formers with different reactivity and many potentially interactive impurities, are difficult to elucidate.

There are three basic steps in the polymerization mechanism:

- Initiation
- Propagation
- Termination

First of all, a clarification of the terminology is necessary. The commonly applied expression "catalyst" is misleading, because usually the substances that induce polymerization are consumed during reaction, which is contrary to the standard definition of a catalyst.

Moreover, the practice of referring to Friedel-Crafts acids as "catalysts" or "initiators" and proton sources as "cocatalysts" or "coinitiators" does not correspond with the real

Table 3.1 Cationic initiating systems

Initiating system	Initiator	Initiating species	Coinitiator	Counteranion
H_2SO_4	H_2SO_4	H^+		HSO_4^-
H_2O/BF_3	H_2O	H^+	BF_3	BF_3OH^-
t-BuCl/Et_2AlCl	*t*-BuCl	*t*-Bu^+	Et_2AlCl	$Et_2AlCl_2^-$
Cl_2/BCl_3	Cl_2	Cl^+	BCl_3	BCl_4^-

mechanism, because the true initiating species is the cationogen, and the action of the Friedel-Crafts acid is to help generate the initial cation.

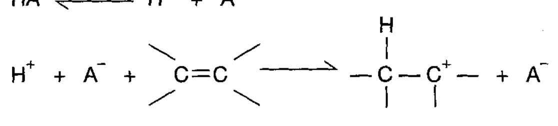
So, according to Kennedy and Marshall cationic sources such as Brønsted acids, or carbonium sources such as organic halides are termed initiators, and Friedel-Crafts or Lewis acids, that assist in the initiation step are termed coinitiators. The term initiating system is applied to the two-component systems composed of the initiating species and the Lewis acid, which determines the nature of the counteranion. Examples of the nomenclature of cationic initiating systems are given in Table 3.1.

Hydrocarbon resins are conventionally produced by adding $AlCl_3$, BF_3, or other Friedel-Crafts acids to a particular feedstock, mostly in the presence of various promoters such as HCl, *t*-BuCl, water, or phenol. Older processes use H_2SO_4 or H_3PO_4.

A simplified representation of the initiation mechanism is given below. For more details see Kennedy and Maréchal [3.1].

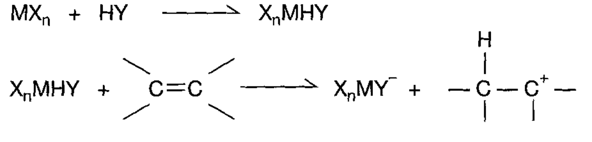
- Initiation
  - by Brønsted acids:

$$HA \rightleftharpoons H^+ + A^-$$

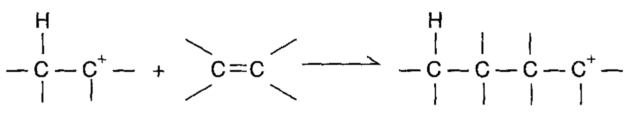


  - by Friedel-Crafts acids:

$$MX_n + HY \longrightarrow X_nMHY$$



- Propagation



In fact, propagation is a rather complex step and very difficult to achieve.

- Transfer

Chain transfer or charge transfer is the process in which the growing carbonium ion transfers its charge and with it its propagating ability to a monomer M, either dicectly

$$\sim C^+ + M \rightarrow [\text{transition states}] \rightarrow \sim C^* + HM^+$$

or indirectly by the intervention of a nucleophilic transfer agent:

$$\sim C^+ + Nu \rightarrow [\text{transition states}] \xrightarrow{+M} \sim C^* + - M^+$$

where:

	C^+	is the growing carbonium ion,
	C^*	is the nonpropagating olefinic, cyclic, or -CH terminus,
	Nu	is a charged or neutral nucleophilic transfer agent,
	M^+	is the new cationic monomer chain carrier.

The characteristic step in this process is the generation of a new propagating unit.

- Termination

Termination consists of the irreversible destruction of the propagating ability of a kinetic chain.

It should be noted that termination and chain transfer are different processes, and must be carefully distinguished.

Termination recations may be of different kinds. In industrial processes, termination is achieved by introduction of a nucleophile:

$$\sim C^+ + Nu \rightarrow \sim C\ Nu^+$$

Examples of commonly used nucleophiles are alcohols, ammonia, amines, alkalis, or simply water.

Kinetic termination of the cationic propagating chain is usually completed long before the quenching agent is introduced. The addition of nucleophiles serves to convert the remaining Friedel-Crafts acids and derivatives to conveniently disposable oxides.

It is obvious that, as little is known, even about one-component resin former systems, it is not possible to obtain exact information about the phenomena that occur in such complicated mixtures as feedstreams.

The most important reaction parameters are:

- Feed composition
- Total and relative concentration of resin formers in the feed
- Type of initiating system and its concentration
- Temperature
- Kinetics (isothermal or adiabatic)

These parameters must be carefully controlled as they affect the reaction in terms of yield, type (polymerization, alkylation), molecular mass, and molecular mass distribution.

In the presence of aluminum halides, the resins formed have higher molecular mass than those produced in the presence of boron trifluoride complexes. The proportion of initiator in the reactant medium influences molecular mass and composition of the resin; high concentrations give resins with lower molecular mass, and lower concentrations give resins with higher molecular mass. A low initiator concentration may influence resin composition by selectivity, i.e., only the most reactive components are transformed. Reaction temperature affects the molecular mass, yield, and color of the product. Molecular mass decreases and yield increases with increasing temperature.

The chosen feed is contacted with the initiating system by vigorous mixing. The reaction is exothermic, and must be strictly temperature controlled. After reaction, the initiating system is deactivated (e.g., by addition of water, alkali, lime, or ammonia). The unreacted feed and the low molecular mass oligomers are then removed by distillation, usually in combination with a steam-stripping process. The residual resin is conditioned in flakes, bulk, or other forms.

Dicyclopentadiene resins are usually manufactured by thermal polymerization of various dicyclopentadiene feedstreams that may also contain styrenes or indenes.

3.1 Aromatic Hydrocarbon Resins

The general procedure in the manufacture of coal tar or petroleum-based aromatic C_9 resins follows basically the same pattern.

Coal-tar feedstreams contain initiator poisons, such as pyridines. These have to be removed before further processing. Petroleum-based feedstreams contain only traces of these impurities, and are generally used without further treatment.

Other pretreatments may be applied in order to improve color, or to adjust the concentration or type of resin formers. This adapted feed is brought into contact with an initiating system, usually BF_3 complexes. The exothermic polymerization reaction must be carefully temperature controlled. The process may be conducted discontinously or continuously.

After deactivation and removal of the initiating system, the resin is separated from solvent and low molecular mass material by distillation.

Modified resins may be obtained by addition of special resin formers to the initial feed, or by subsequent reactions on the final resin, e.g., hydrogenation.

3.1.1 Pretreatment of Raw Material

Coal-tar light oils from primary tar distillations contain 3–10 % phenols and 2–7 % pyridine bases. Both have to be removed prior to further processing. Their recovery is of commercial interest, and in resin manufacture the tar bases significantly impede the action of the initiating system in the polymerization process.

Phenols are recovered in a batch or continuous extraction process with dilute sodium hydroxide solution (10 %), the pyridine bases by washing with dilute sulfuric acid (30 %). The so-called washed light oil obtained at this stage can be stored in normal steel tanks.

Another unwanted impurity sometimes present in the coal-tar light oil fractions is benzonitrile (2–3 %), which may be removed by saponification with sodium hydroxide.

Following extraction, the washed coal-tar light oil is subjected to a final distillation in order to

- concentrate the unsaturated compounds
- separate and recover commercially interesting nonpolymerizable neutral compounds.

In this rectification, the following fractions are taken off:

- Benzene/toluene/xylenes (BTX fraction)
- Coal-tar light naphtha (high in unsaturated compounds)
- Coal-tar heavy naphtha (heavy benzene homolog fraction)
- Distillation residue (naphthalene-containing bottoms)

The coal-tar light naphtha, in which the monomers for resin production are concentrated, is passed to intermediate storage tanks.

Some companies take off two (or more) separate partial cuts, one with a somewhat lower indene content, though still perfectly suitable for resinification, yielding resin grades of medium or dark color and lower softening points. A second partial cut with a higher indene concentration is suitable for making high-quality resins of lighter color and medium to extremely high softening points. The monomer (indene) content during the fractionation process can be monitored by GLC or measuring the refractive index, comparing with standard samples.

Petroleum-based resin oils recovered from cracker bottoms do not contain significant quantities of phenols or pyridine bases, and thus are normally passed directly (without any washing) to fractionated distillation. Compared with coal-tar-derived streams petroleum-based oils offer more flexibility in producing special resin feedstreams, for example by more or less eliminating styrenes or indenes in the distillation step.

The following fractions of petroleum-based C_9 resin oil may be distinguished:

- Benzene/toluene/xylenes (BTX fraction)
- α-Methylstyrene/vinyltoluenes fraction
- Indene fraction
- Methylindene fraction
- Petroleum heavy naphtha (high-boiling benzene homologs, etc.)
- Distillation residue (naphthalene-containing bottoms)

In some cases, however, petroleum- or coal-tar-based materials can be pretreated in a separate additional process step to improve the color of the final resin.

To accomplish this, the resin feedstock can be treated with small quantities of, e.g., sulfuric acid (other Brønsted or Friedel-Crafts acids may also be used) under strictly controlled mild conditions. In this procedure, unwanted impurities, mainly small quantities of CPD/DCPD, are reacted and thus removed or reduced. After neutralization and distillation, polymerization gives resins with improved color. Further improving treatments may be applied, e.g., with activated carbon or with bleaching clay. In fact, the actual upgrading method is generally regarded as an industrial secret by the manufacturer.

Intermediate storage time of resin raw material should be kept to a minimum to avoid any reactions of this oxidation-sensitive material, to prevent discoloration and unwanted thermal reactions. Tanks may be protected with neutral inert gases. Addition of antioxidants may also be helpful.

3.1.2 Polymerization

Basically the polymerization process of these aromatic resin feeds, either from coal tar or petroleum fractions, are the same and may be run either batchwise or continuously.

Batch runs are particularly indicated for production of smaller quantities of speciality resins, and also in case of fluctuating raw material quality, as individual operation conditions can be adapted to each run. Continuous processes are well suited to produce bulk standard and speciality resins, but require high consistency of feedstock.

Temperature is a most valuable parameter for molecular mass control: molecular mass increases with decreasing reaction temperature and decreases with increasing temperature. Molecular mass distribution is influenced by temperature variation: isothermal polymerization gives narrower molecular mass distribution than batch polymerization, where temperatur increases from the starting temperature to a desired end temperature.

The most important factors allowing production of various resin types are:

- Choice and upgrading of resin feed with adjustment of resin former types and feed blending
- Concentration of resin formers
- Process conditions, mainly temperature and residence time

Some key qualities of the resins are controlled by the styrenes/indenes ratio, and their methylated homologs, which may be adjusted by distillation. In this respect petroleum-based feed offers more flexibility as it contains more styrenes than coal-tar-based feed (see Section 2.2).

Earlier resinification processes for the production of indene- coumarone resins were based on sulfuric acid in batch runs as described below:

Sulfuric acid is added to the stirred resin feedstock at a temperature of ca. 20–35 °C. Quick and thorough dispersion of sulfuric acid is important to avoid "burning" (scorching) leading to dark-colored resins. The temperature rise of the exothermic reaction must be closely controlled.

Modern processes conventionally use BF_3 as gas, or its complexes with ether or phenol. Use of aluminum chloride is less popular in the production of aromatic resins. Figure 3.1 gives a general view of the different process steps.

3.1.2.1 Batch Polymerization

In the batch process, the reaction mixture passes through a wide temperature range, from the initial starting temperature of ca. 20–50 °C up to final temperatures of ca. 130–180 °C, depending on monomer types (and hence reactivity) and concentration in the feed, forming polymer molecules of different length. A wide molecular mass distribution is typical of this type of polymerization (Fig. 3.2).

Lower starting temperatures give lighter-colored and harder resins, whereas higher starting temperatures give lower softening points and slightly darker colors.

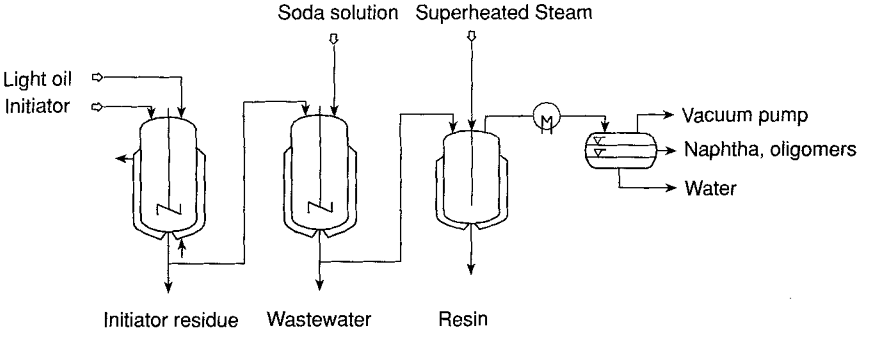


Figure 3.1 Manufacture of indene-coumarone and aromatic petroleum based resins

3.1.2.2 Continuous Polymerization

This process type is designed for the production of commodity type and speciality resins using highly consistent feedstocks. This continuous isothermal polymerization yields resins with a relatively narrow molecular mass distribution. This indicates that the resins will have good solubility and compatibility characteristics. A process scheme is given in Figure 3.2.

Polymerization is carried out at a fixed temperature that is strictly controlled throughout the whole polymerization step. The temperature is controlled by the addition rate of the intiating system and, if necessary, by external cooling.

The softening point of the final resin is mainly determined by appropriate selection of the constant temperature level and the concentration of the initiating system, and follows the previously described general rules.

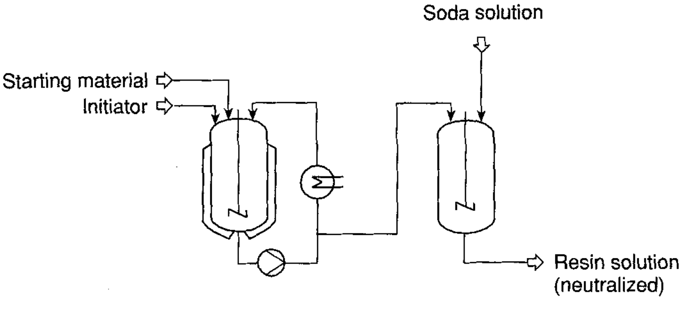


Figure 3.2 Continuous isothermal polymerization

Polymerization in a tube reactor (Fig. 3.3) is best suited for the production of bigger lots from uniform starting materials in isothermal or non-isothermal processes.

Tube length is calculated to assure sufficient residence time and can be up to 200 m or more.

The feed, with maximum monomer concentration of 50 %, is preheated to an initial temperature of ca. 40–70 °C for hard resins, and ca. 100–110 °C for soft resins. Final temperatures are in the range 130–180 °C for hard and ca. 200 °C for soft resins.

The initiating system, normally BF_3 etherate, is injected through a nozzle, situated a short distance from the feed inlet. The tube system is jacketed for cooling with water or thermal oil, if required, to control the exothermic reaction. After reaction the polymerizate passes to deactivation and further processing.

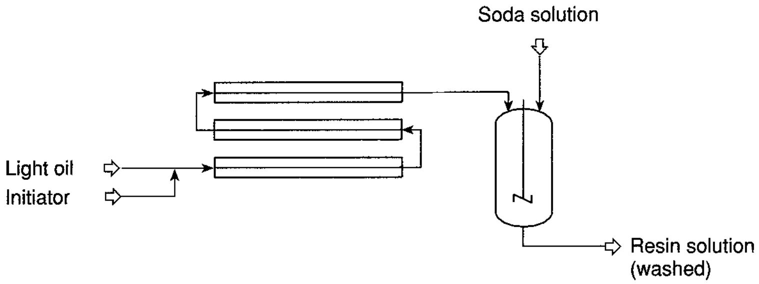


Figure 3.3 Polymerization in a tube reactor

3.1.2.3 Cascade Reactor Polymerization

This two- or multistep continuous polymerization process (Fig. 3.4) is conducted in the same manner as the standard isothermal procedure described in Section 3.1.2.2. However, installation of two or more reaction vessels allows operation at two or more constant temperature levels, resulting in a higher resin yield and a narrower molecular mass distribution of the final resin.

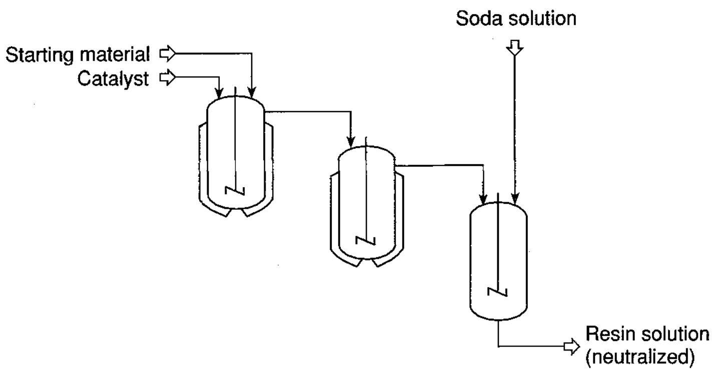


Figure 3.4 Isothermal polymerization in a cascade reactor system

3.1.3 Deactivation

Deactivation is achieved by adding a nucleophilic quenching agent to the reaction mixture in order to convert residual Friedel-Crafts acids and derivatives to conveniently disposable species. Commonly used nucleophiles are ammonia, amines, alcohols, alkalis, or simply water, e.g., aqueous sodium hydroxide solution (15–20 %), a soda solution (15–17 %), calcium hydroxide as a solid or as suspension, limestone, superheated steam.

Deactivation may be executed batchwise or continuously, depending on the overall process type.

A liquid deactivation medium can be separated from the polymerizate by simple phase separation, a solid medium by filtration, e.g., over a fixed-bed filter device. The filtration residues have to be discarded and disposed of in a controlled chemical dump.

3.1.4 Intermediate Storage of Neutralized Polymerizates

In discontinuous processes polymerizates are sometimes stored before separation of the resin by distillation. These polymerizates are very sensitive to oxidative attack, resulting in discoloration and other quality degradation. The presence of rust favors degradation (Fig. 3.5).

To avoid quality problems, the following preventive measures are indicated: use of high-quality steel alloys for tanks and piping, protection with an inert gas, addition of low volatile antioxidants, and reducing storage time to a strict minimum.

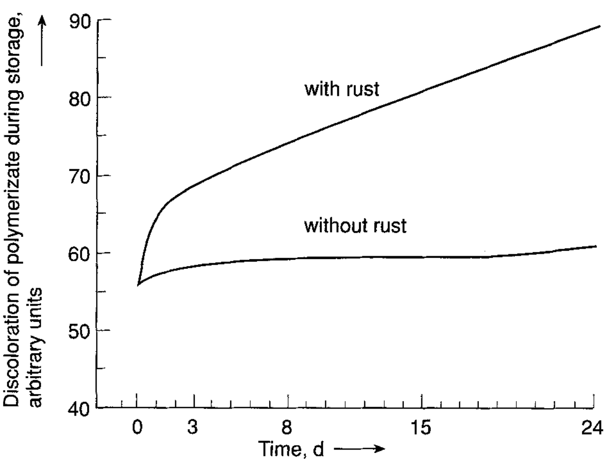


Figure 3.5 Effect of rust on polymerizate degradation

3.1.5 Resin Separation from Unreacted Feedstock

Polymerizates contain ca. 40–50 % of saturated hydrocarbons, together with a certain percentage of low molecular mass polymers (oligomers). These materials are separated by distillation.

The standard vacuum distillation used to remove unreacted material may be followed by a steam-stripping step to drive out the remaining solvent, monomers and, if present, light oligomers. At this stage, the softening point of the final resin may be adjusted by taking off defined amounts of oligomers. Removal of these relatively low-boiling materials is important because:

- remaining low oligomers act as softening agents (internal plasticizers) and lower the softening point to an unacceptable level
- low oligomers have a characteristic intense odor, so their removal is very important, especially for resins in some adhesive applications, e.g., hot-melts.

The low molecular mass oligomers recovered may be used to make lower softening point resins by blending with harder resins under controlled conditions for uses where odor is not a problem.

Stabilizers (antioxidants) may be added to the liquid resin while it is still hot to inhibit further oxidation (discoloration and odor).

The final resin may be conditioned by discharging into drums, or more usually, by conversion to chips or pastilles.

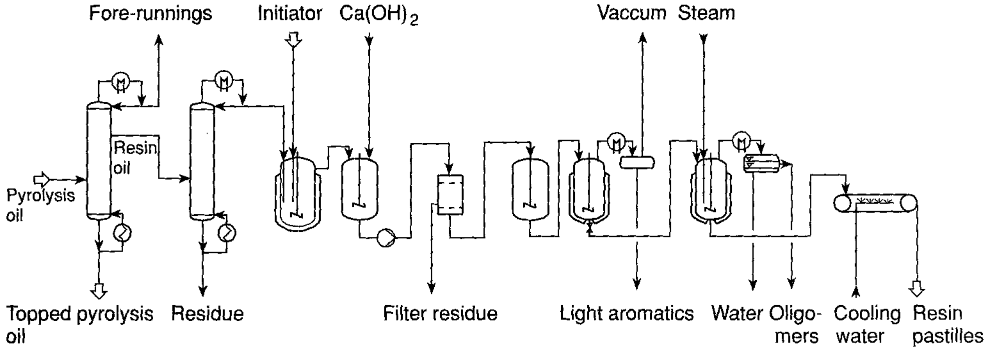


Figure 3.6 Complete processing scheme for resin manufacture

There is a wide range of unmodified indene–coumarone and C_9 hydrocarbon resins available. Their specific characteristics depend on the feedstocks and manufacturing techniques:

- Indene–coumarone resins:
  Softening point range: liquid to 170 °C R & B, color: Gardner 5-9

- Standard C_9 (full range) resins:
  Softening point range: liquid to 125 °C R & B, color: Gardner 6–11
- Adaptable C_9 resins:
  Softening point range: 65 to 170 °C R & B, color: Gardner 5–10
- Partial fraction C_9 resins:
  Softening point range: liquid to 125 °C R & B, color: Gardner 6–10

3.2 Manufacture of Resins from Technically Pure Aromatic Monomers

Very light colored hydrocarbon resins are produced from commercially available high-purity aromatic monomers, such as styrene and its alkylated homologs. Such monomers or blends respond well to carbocationic polymerization in the presence of initiating systems based on boron trifluoride, ethylaluminum dichloride, diethylaluminum chloride, and acid clay.

A wide variety of such resins is on the market. They are based on pure monomers such as styrene, α-methylstyrene, vinyltoluenes, and blends of these. Resins made from blends of styrene and terpenes, or styrenes with aliphatics such as isobutene, are also available.

Production processes for these resins are basically the same as for aromatic resins from the various feedstreams described previously. As the raw material does not contain impurities (catalyst poisons) which occur in coal tar or petroleum-based feedstreams, smaller portions of initiating systems are sufficient. The manufacturing process can be batchwise or continuous.

3.3 Aliphatic C_5 Resins

The starting material for the production of these resins comes from petroleum C_5 streams, containing straight-chain and cyclic molecules, mono- and diolefins, but no aromatics. Composition of the feedstock is of great importance, and varies from source to source. Resins can be produced with a wide range of desirable properties, depending on raw material, addition of modifying monomers (monoolefins, terpenes, aromatics), and operating conditions.

The most commonly used initiator system is based on aluminum chloride. A complex with hydrochlorid acid, dissolved in an appropriate solvent, e.g., xylene, is highly effective. When using solid aluminum chloride, the quality and particle size of the aluminum chloride, which is fed into the reactor through a special inlet device, are of major importance and are usually kept secret by manufacturers.

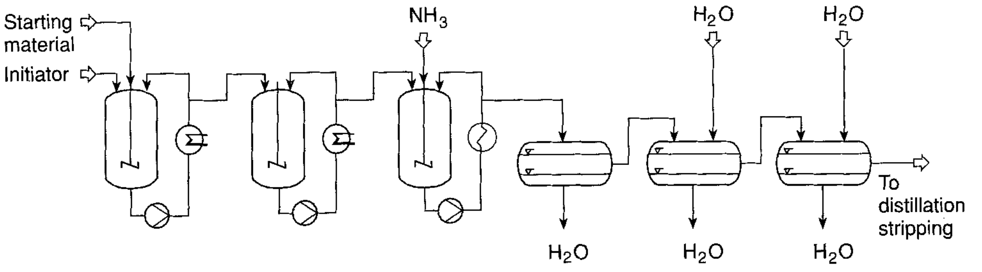


Figure 3.7 Polymerization of a C_5 stream

The efficiency of Friedel-Crafts initiators are approximately as follows:

$$AlCl_3 = AlBr_3 > TiCl_4 > BF_3 \text{ etherate}/H_2O > SnCl_4$$

A typical example of production process is given in the following description of a continuously operated isothermal process (Fig. 3.7).

The resinification is commonly executed in a two-stage polymerization, with most of the subsequent processing steps also involving more than one stage. A strictly controlled stream of the resin feedstock, blended with an appropriate portion of saturated compounds as thinner, is fed into the first reactor. The temperature of the material is normally kept at 45 °C on average. The reactors and the other vessels have to be capable of withstanding working pressures of up to 10–11 kg/cm^2.

The total reaction time is ca. 4h. Part of the reactor content is recycled, a part is fed into the second reactor stage for completion of the reaction. Complete polymerization of the monomers is necessary as otherwise the later separation process is rendered more difficult.

The polymer solution from the second reactor stage is passed to the neutralization vessel which is kept at a relatively high temperature. The means of deactivation (neutralization) is gaseous ammonia.

Following the deactivation step, the resin solution is passed to a settling tank. After that, the material is treated with water in a multi-stage scrubber system. From there, the resin solution is passed to the further processing steps (distillation etc.), identical to the process for aromatic resins.

Initiating systems for the production of resins based on piperylene concentrates may be alkyl aluminum, titanium halide, alkyl lithium, or boron trifluoride. Anhydrous $AlCl_3$ systems are the most widely employed. Comonomers such as isobutene, butadiene, methylbutenes, or styrenes may be added to the initial feedstream to adjust the final resin properties to individual uses.

By taking off low molecular mass oligomers at the final steam distillation stage, the softening points may be adjusted. Resin types manufactured in this process are shown in Table 3.2

Table 3.2 Classification of C_5 hydrocarbon resins

Resin type	Softening point, °C R & B	Color, Gardner
Unmodified		
General purpose	100	5–7
Improved	95	5–7
Premium	80–100	3.5–5
Modified		
Cyclic-modified	115	5
Aromatic-modified	liquid to 90	5-9
Cyclic/aromatic-modified	95	3

3.4 Dicyclopentadiene Resins

As already discussed in Section 2.2.3, CPD/DCPD resins are manufactured from steam-cracking by-product streams containing substantial amounts of dicyclopentadiene. The DCPD content of the stream is the basis for the cycloaliphatic structures predominant in this group of resins. The balance of the unsaturates in the starting material are codimers of cyclopentadiene, together with other dienes.

In contrast to the catalytic polymerization type described previously, polymerization of DCPD streams is thermal in character.

Dicyclopentadiene streams containing at least ca. 35 % of dicyclopentadiene respond well to thermal polymerization. Initiated by heating, the reaction is very exothermic, and the temperature must be carefully controlled.

Addition of aromatic unsaturated material, such as styrene, α-methylstyrene, vinyltoluene, or aromatic fractions is usual. Their presence reduces the heat of reaction, and allows modification of the properties of the final resins.

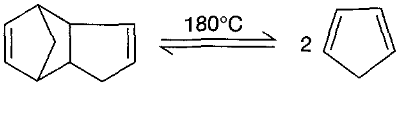
It is important to differentiate between two lines of DCPD-based resins:

- DCPD resins with a substantial amount of aromatic unsaturated components, representing an intermediate type with medium bromine numbers of ca. 55–75, i.e., a higher degree of reactivity compared with standard, hydrocarbon resins having bromine numbers in the range of ca. 10–45
- DCPD resins with a predominance of DCPD, showing higher bromine numbers of ca. 65–100 and even higher, which are distinctly heat- and oleo-reactive.

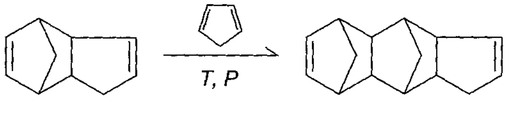
Resins of the first type can be produced, e.g., when using an α-methylstyrene/vinyltoluene cut from a C_9 resin oil as diluent in the polymerization reaction.

The polymerization of DCPD streams is a pressure/temperature (P/T) reaction requiring no catalyst. This P/T reaction may follow the below described scheme:

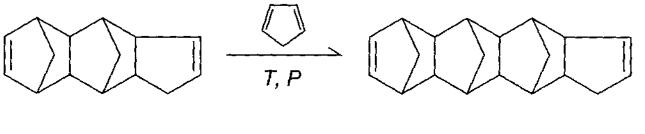
1) Splitting of DCPD to CPD



2) Cycloaddition of CPD to the norbornene ring of DCPD



3) Cycloaddition of CPD to the growing chain



On average, a 50–60 % DCPD stream is used in making DCPD resins. When using highly concentrated DCPD fractions as starting material, the *P/T* reaction has to be carried out in the presence of an aromatic or aliphatic solvent as diluent. It is of advantage to select solvents having a relatively high flash point as they lead to a low solvent viscosity of the resin solution and to a low reaction pressure for the *P/T* polymerization. Amongst others, xylene, naphtha, mineral spirits 140/160, and similar materials are used.

Polymerization temperature and reaction time have to be matched to each other to facilitate splitting of DCPD to CPD and the subsequent resinification process, and to avoid subsequent crosslinking, which may occur owing to the reactivity of the DCPD resin at elevated temperatures, leading to unwanted insoluble products. Strict monitoring of the temperature is, therefore, absolutely necessary. In this context, the evolution of heat (heat of transformation) is of great importance in the *P/T* polymerization. At the average manufacturing conditions, the heat of polymerization is in the range 200–300 kJ per kilogram of starting material (e.g., 60 % DCPD in xylene).

A typical example of DCPD resin manufacture (Fig. 3.8) is as follows: After blending the DCPD stream with a diluent if required, manufacture, executed in pressure equipment, usually starts with preheating the starting material to ca. 50–60 °C. The actual polymerization process is executed by increasing the temperature in two or three steps. A certain holding time at the different temperature stages is effected, with the pressure automatically increasing in line with the increasing temperature. The end temperature must not exceed 280 °C. Exact temperature control, especially between 200 and 280 °C, is highly important to prevent subsequent reaction of the polymerizate, e.g., too high a temperature may lead to decomposition of the reaction mixture (explosion). Heating and holding time may vary widely, depending on specific plant and processing conditions, but nevertheless the figures quoted give a rough idea of the system.

The resulting softening points depend on the polymerization conditions, but also on the conditions of the distillation and stripping stages later in the process.

After completion of the polymerization, taking in total ca. 15–17 h, the charge is depressurized, and the material passed to the subsequent distillation and steam-stripping facilities for further processing. Instead of the discontinuous steam-stripping process a continuously operated thin-layer evaporator can also be used. The very mild operating conditions of this method reduce thermal stress on the resin.

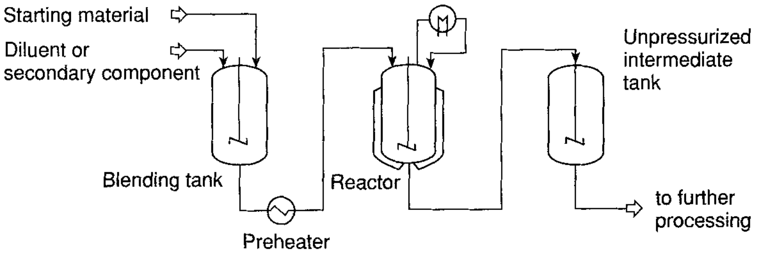


Figure 3.8 Manufacture of DCPD resins

The color of the final resin is subject to thermal stress during the entire manufacturing process, and depends in particular on the level of peroxidation of the starting material. Apart from the general polymerization conditions, it is the variation of the distillation/ evaporation conditions (vacuum, evaporation temperature, stripping steam temperature, stripping time) which broadly determine the softening point. By recycling the distillate, it is possible to increase the overall yield of resins considerably.

The cycloaliphatic, unsaturated resin types manufactured in the above described process comprise resins with softening points of 30 to 120°C R & B, Gardner colors 5 to 6, and iodine numbers ranging from ca. 95 to 175.

3.5 Modified Resins

Use of the term "modified" resin is somewhat arbitrary; it is often used to distinguish resins made from straight distillation runs from those based on:

- Streams modified by blending with distinct monomers or fractions
- Streams modified by subsequent reaction of the finished resins, e.g., hydrogenation, or reaction with other reactive compounds, e.g., maleic anhydride

Physical mixtures of resins, e.g., hydrocarbon resins with rosin or rosin derivatives are also on the market and may be classified as modified resins (blended resins).

In view of the wide modification possibilities, only a general summary can be given in the following, illustrated by a few specific examples.

3.5.1 In Situ Modification

The resin profile may be adapted to specific applications by copolymerization of the initial feedstream with other unsaturated monomers, concentrates or fractions. By adding styrene to the indene–coumarone fraction, the penetration depth is improved – a desirable property in resins for floor tiles. By mixing indene concentrates or dicyclopentadiene fractions with C_9 streams, resins with high softening points, useful for ink manufacture,

may be produced. Introduction of aliphatic properties in aromatic resins is obtained by polymerization of mixtures of C_9 streams with isobutene, C_5 concentrates, or terpenes. Such resins have improved solubility and compatibility characteristics, useful e.g., in adhesives and rubbers. By addition of phenol to C_9 feedstock, resins with a certain hydroxyl content, compatible with epoxy and polyurethane resins, can be manufactured. Aliphatic feedstreams, particularly piperylene concentrates, may be modified by addition of monoolefins, such as methylbutenes, isobutene, styrene, and α-methylstyrene, leading to resins with lower unsaturation, better stability and color. Tackifying properties may also be improved. Other modifying agents are terpenes, such as α-pinene, β-pinene, and limonene, sometimes used together with aromatic monomers, such as styrene and α-methylstyrene. The resulting resins exhibit high tackifying properties.

DCPD streams, when modified with aromatic olefins or streams containing them, yield resins with high softening points and good solubility. The following examples are an arbitrary choice and serve only as illustrations.

3.5.1.1 Styrene-Modified Aromatic Resins

For some special applications, styrene-modified indene–coumarone resins show better performance compared with unmodified standard IC resins. A typical example is their use in formulating floor tiles. Immediately after World War II, indene–coumarone resins were widely used in the manufacture of floor tiles. As a matter of fact, this application was one of the major outlets for most IC resins at that time, and even today IC resins and C_9 hydrocarbon resins still find some use in that area, especially in a number of overseas countries, although the quantities used are comparatively small.

The major reason for using modified IC resins were the distinct, clearly visible indentations observed in floor tiles due to the pressure of women's footwear with pointed heels (stiletto heels and similar), because of the relatively high pressure on the flooring material.

In order to cope with this problem, IC resin copolymerizates with 7.5, and 15 % styrene have greatly improved indentation resistance.

The starting material for producing IC resins is copolymerized with the selected corresponding percentage of styrene under the normal manufacturing conditions used for standard IC resins. The resulting styrene-modified indene–coumarone resins have a higher solution and melt viscosity, compared with the unmodified standard resin. The positive effect of this modification on penetration values is given in Table 3.3.

Table 3.3 Indentation hardness data for styrene-modified indene-coumarone resins

Softening point, °C	Styrene content, %		
	0	7.5	15
	Penetration, mm		
100	26–28 (65 °C)	20–22 (65 °C)	8–10 (65 °C)
120	16–18 (80 °C)	10–12 (80 °C)	1–2 (80 °C)

It should be mentioned that this improvement in indentation resistance may also be obtained by incorporation of polystyrene of appropriate molecular mass.

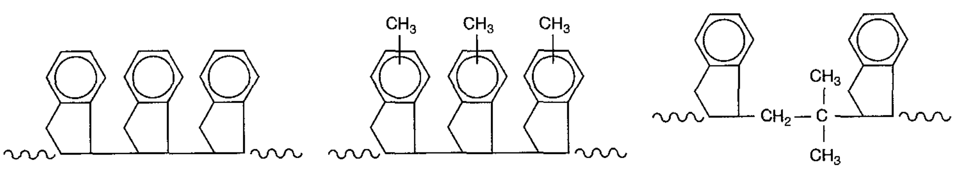
There are also C_9 resins on the market with relatively high styrene contents, generally produced from selected styrene-rich raw material (normally C_9 feed does not contain high styrene concentrations). These resins seem to show a lower performance in the floor tile industry than the previously described types, possibly because of the lower indene content.

3.5.1.2 Aliphatic-Modified Aromatic Resins

By blending C_5 and C_9 refinery streams, C_5/C_9 copolymer resins, also referred to as C_5/C_9 hybrids, can be obtained.

As might be expected, this type of in situ copolymer exhibits properties and performance intermediate between aliphatic C_5 and aromatic C_9 resins. In practice, this C_5/C_9 copolymer is preferred to a mixture of C_5 and C_9 resins.

Another example of modified resins is the copolymerization of aromatic feedstreams with isobutene, which produces resins with properties very close to those of resins containing high methylindene concentrations, mainly with regard to solubility and compatibility.



Indene resin Methylindene resin Indene/butene resin

Manufacture of these resins may follow the same procedure as the continuous, isothermal process for making C_9 petroleum-based resins.

3.5.1.3 Terpene-Modified Aromatic Resins

While the solubility of standard IC resins in aromatic solvents is excellent, their solubility in mineral spirits is not satisfactory, especially when nonisothermally produced IC resins are used. Indene–coumarone resins manufactured by an isothermal process show better solubility, coming close to that of C_9 hydrocarbon resins.

Another possibility is to make an aromatic resin from the high-boiling cut of a coal-tar-based raw material stream, using a special fraction in the boiling range of 4-methyl indene (205–215 °C). This yields a resin with a mineral spirit solubility comparable to a C_9 petroleum-based resin. The total quantity is rather limited, and this method is not of commercial interest.

Improved properties with regard to solubility and compatibility may be obtained by introduction of terpenes in the original aromatic feedstream. A method of improving

solubility in mineral spirits came into use after World War II - copolymerization with terpenes. As the availability of cheap, isolated, single terpenes for this purpose was limited, the copolymerization partner chosen was technically pure dipentene, the racemate of D- and L-limonene, obtained in upgrading of turpentine oil.

By copolymerization of 10 % dipentene with indene-coumarone starting material, a mineral-spirit-soluble IC resin can be produced, with a cloud point between 0 and -15 °C (see Section 4.2.14.1 for discussion of cloud point). As this cloud point level is unsatisfactory for most purposes, a higher percentage of dipentene must be copolymerized. With higher amounts of dipentene, the comparatively low reactivity of the technical grade dipentene or some of its constituents may render the resins too soft, i.e., standard resins with softening point 100 °C R & B cannot be manufactured in that way. The reason for this is the widely varying composition of the technical grade dipentene on the market, depending on source, variable concentration of the constituents, and differing reactivity. Though the search for an optimum dipentene type is mainly empirical, some general principles are worth mentioning:

- high total content of reactive constituents
- high β-pinene content, low α-pinene
- more dicyclics than monocyclics
- relatively high concentration of carene

To make a dipentene-modified IC resin with a suitable technical grade dipentene the normal procedure for producing IC resins is modified. It is preferable to perform the polymerization in two steps: the first polymerization step is started with one-third of the total catalyst quantity, at 95 °C. The exothermic reaction increases the temperature to ca. 130–140 °C. In a second step, the reaction mass is first cooled down to 20 °C, after which the polymerization is continued by adding the other two-thirds of catalyst, with the temperature again rising to 60–70 °C. This procedure gives a resin of light color and a cloud point in mineral spirits below -15 °C. A subsequent ripening process has also proved useful in increasing the resin yield.

It goes without saying that it is easy to copolymerize indene–coumarone feedstocks with isolated pure terpenes. However, with the wide range of C_9 and C_5 hydrocarbon resins on the market nowadays, it no longer makes sense to manufacture resins combining the characteristics of terpenes with those of indene–coumarone resins.

3.5.1.4 Phenol-Modified Aromatic Resins

Standard indene–coumarone resins, as well as C_9 hydrocarbon resins are completely hydrocarbon in nature and devoid of functional groups. The phenol-modified IC resins are unreactive thermoplastic resins, but they differ with respect to the hydroxyl groups introduced into the resin molecule through the phenol. They may vary in character, depending on the hydroxyl group concentration and the degree of inhibition of the chemical reactivity of the functional group.

The reaction mechanism and the way in which the phenol is incorporated in the polymer molecule has not yet been fully elucidated.

Phenol-modified resins may also be referred to as alkylated phenolic resins, with indene being the major alkylating component. They are soluble in alcohols, glycols, glycol ethers,

esters, and ketones. Owing to their content of phenolic hydroxyl (OH) groups, they have a higher acid number (0.5–1) compared with standard IC resins (0). They do not contain any free phenol.

As a significant characteristic, the markedly better solubility and compatibility must be mentioned. For instance, on the subject of alcohol solubility of this type of resin, it should be noted that the solubility depends to a large extent on the softening point of the resin, and on the water content in the alcohol. Solubility decreases as the softening point increases and, because of the hydrophobic nature of IC resins, it decreases as the water content of the alcohol increases.

Alcohol solubility of the phenol-modified resins is increased considerably by adding further solvents to the mixture, e.g., a small quantity of glycols.

Through the phenol modification the resin acquires are more polar nature, which makes it suitable for using in adhesives. In addition, its solubility in alcohol leads to its inclusion in certain adhesives for floor coverings, for which solvent mixtures containing alcohol are frequently made.

For the manufacture of the phenol-modified IC resins, it is necessary to select a starting fraction with a comparatively high indene concentration, ca. 55–60 %, because the modified resin tends to act as an internal plasticizer, and reduces the softening point of the resulting resin when the starting material is not properly chosen. On average, ca. 10–15 % phenol are incorporated in the final resin. The starting temperature of the polymerization should be low, the end temperature in the range of 130 °C. It is also advisable to chose a longer steam-stripping time of minimum 6 h or more instead of the commonly used 4 h, in order to minimize the content of the odor-intensive oligomerics. Generally it can be said that the method of producing phenol-modified indene–coumarone resins follows the normal lines.

This type of modified resin is mostly available in the medium softening point range, the most popular grade having a melting point of 90 °C R & B. The highest softening point available is ca. 130 °C R & B, but this resin shows a distinctly lower alcohol solubility compared with the 90 °C R & B resin, for reasons explained above.

It has already been explained that changing the polymerization procedure from non-isothermal to an isothermal process improves the general solubility and compatibility characteristics. The same effect can be reached by modifying non-isothermally produced C_9 resins with a limited quantity of phenol. The manufacture follows exactly the same scheme as for phenol-modified indene–coumarone resins, and is therefore not described here. The only difference is in the quantity of phenol incorporated in the polymer which is only 3–3.5 %. In effect, even slight modification with phenol is sufficient to show clearly improved data with regard to solubility and compatibility for this resin group, which generally have softening points of 100–120 °C R & B. For example, a distinctly improved compatibility with medium- and long-oil alkyds, and even with some short-oil alkyds can be observed. The enhanced solubility, for instance in a number of mineral oils used in temporary rust protection, is also worth mentioning.

3.5.2 Modification of Finished Resins

The main modifications applied to hydrocarbon resins are hydrogenation or reaction with unsaturated organic compounds. Dicyclopentadiene, aromatic, and terpene resins are partially or totally hydrogenated to very lightcolored or even water-white resins. They are especially useful in adhesives, where color and color stability are indispensible.

Reaction with unsaturated organic compounds such as maleic anhydride, unsaturated acids or rosin, are generally applied to the highly unsaturated DCPD resins, for use in the printing ink industry (see Section 5.4), for example. Some examples are given in the following.

3.5.2.1 Hydrogenated Hydrocarbon Resins

Hydrogenation of resins leads to very light-colored or water-white resins with remarkable stability to light and heat. Hydrogenation of resins such as dicyclopentadiene, aromatic, or terpene resins, is carried out under pressure at high temperature in the presence of, e.g., Ni-based catalysts in discontinuous or continuous processes. Attention must be paid to the sulfur content of the resin, as it acts as a catalyst poison. This is especially the case with aromatic resins.

The largest volume of hydrogenated resins is based on dicyclopentadiene resins. A simplified scheme is given in Figure 3.9 [3.2].

Typical dicyclopentadiene resins, with softening points in the range 80–120 °C R & B, Gardner color ca. 9, and bromine value 50–70, are dissolved in an appropriate saturated hydrocarbon solvent. The reaction is carried out in a fixed-bed catalytic reactor. The reaction mixture is transferred to a first tower, where excess hydrogen and solvent is separated. The solvent is recycled. In a second tower, low molecular mass polymers generated by hydrocracking, are eliminated by steam-distillation. The catalyst is a specially developed system based on metals of group VIB and VII; the temperature is 215–270 °C, pressure 40–60 bar, and residence time between 30 min and 3 h.

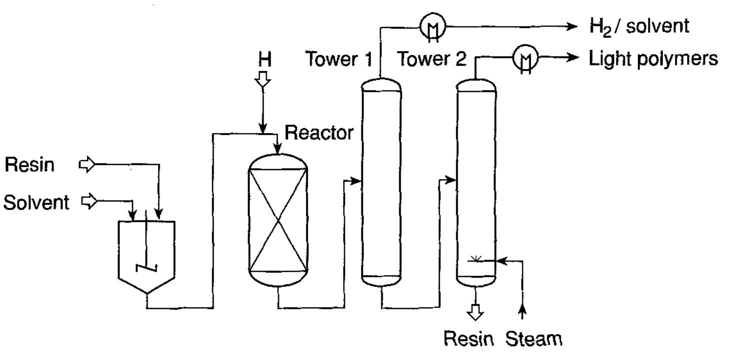


Figure 3.9 Manufacture of hydrogenated resins

The resulting resins have softening points of 80–130 °C R & B, Gardner color < 1, and bromine number < 4.

3.5.2.2 Maleic Anhydride-Modified Resins

A typical dicyclopentadiene resin with a softening point of 148 °C R & B is heated together with ca. 10 % of maleic anhydride for 3 h at ca. 200 °C. The resulting resin has a softening point of 180 °C R & B and an acid number of 53. These resins may undergo further reaction, e.g., esterification.

3.5.2.3 Rosin-Modified Resins

This resin type is mostly based on a DCPD resin, and contains about 30 % rosin. Heating DCPD resins with rosin esters leads to ill-defined and rather complex reactions. The following reaction mechanism has been suggested:

The conjugated double bonds in levopimaric acid (formed as an intermediate step by isomerization) may subsequently undergo a Diels-Alder reaction with the unsaturated part of the DCPD resin. Partial decarboxylation may reduce the acidity of the final resin.

3.6 Polyterpene Resins

The most commonly used terpenes in resin production are α-pinene, β-pinene, and dipentene (DL-limonene). Different initiator systems have been evaluated; the order of effectiveness is:

$AlCl_3 = AlBr_3 > ZrCl_4 > AlCl_3O(C_2H_5)_2 > BF_3O(C_2H_5)_2 > SnCl_4 > SbCl_3 > ZnCl_2$

$AlCl_3$ is the most commonly used initiator, $TiCl_4$ gives resins with very light color, and $AlBr_3$ provides the highest melting points. For dilution, aromatics, such as xylene or toluene, or aliphatics may be used. A typical production process is shown in Figure 3.10.

The terpene, a diluent, and $AlCl_3$ are continuously introduced in the first stirred reactor; the temperature is maintained at 30–50 °C by cooling. About 90 % of reaction is achieved at this stage. The reaction mixture is continuously transferred to a second reactor to finish the reaction. The initiating system is deactivated by vigorous mixing with water. After phase separation and further washing, the organic layer is transferred to vacuum distillation to take off the diluent. At this stage the softening point may be adjusted by taking off the low molecular mass dimers and trimers.

As polyterpene resins are very susceptible to oxidation because of the presence of tertiary carbons, care has to be taken by application of inert gas in the production process and protection of the final resin by application of antioxidants.

Because of the high reactivity of terpenes, a wide range of modifying monomers may be used, i.e., styrenes, piperylene, and isoprene.

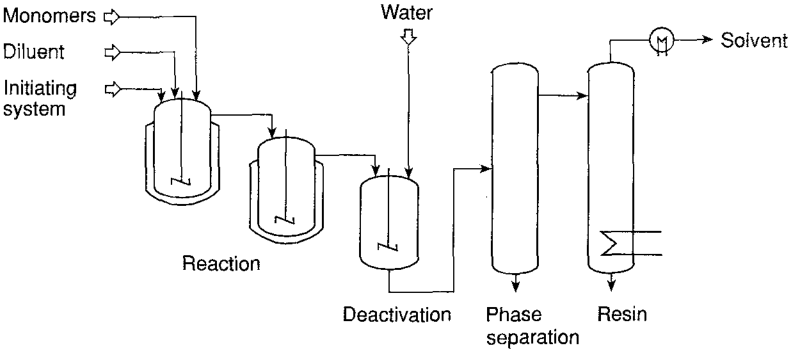


Figure 3.10 Manufacture of polyterpene resins

3.7 Polybutene Resins

These liquid resins, based on petroleum C_4 streams, are produced by cationic polymerization, mainly in the presence of $AlCl_3$ at relatively low temperature.

The precooled feedstream and the initiating system are introduced continuously in a stirred vessel; the temperature should be between -30 and +80 °C. The temperature is maintained by cooling or refluxing. Temperature and $AlCl_3$ concentration are important factors as they influence molecular mass and hence the viscosity of the final resin. After reaction, the mixture is treated with deactivation agents such as water, methanol, ammonia, amines, or aqueous sodium hydroxide. The organic layer, after removal of residues, passes to the distillation section, where solvent and unconverted material is eliminated. In a second stage, low molecular mass polymers may be removed to regulate molecular mass and viscosity.

3.8 Liquid Resins

Liquid resins, solvent-free oligomers, are produced from monomers which may be aromatic, aliphatic, or terpenic, from coal tar or petrochemical feedstreams, or from pure monomers. Two basic types are available: low molecular mass neutral hydrocarbon oligomers, and oligomers containing polar groups (OH), sometimes referred to as "activated" types.

The production process for these resins may be batchwise or continuous, at elevated temperatures and relatively high initiator concentrations. The usual initiators may be used. To obtain the hydroxyl-modified resins, polymerization is carried out in the presence of varying amounts of phenol to yield resins of variable hydroxyl content.

Liquid resins are used mainly as plasticizers and tackifiers. The aromatic polar types are especially designed for use in polar systems such as epoxy-, polyurethane- or polysulfide-based formulations.

3.9 Delivery

The final resin may be conditioned by pouring into drums, or, more usually, it is chipped or pastillized and packed in paper or plastic bags and shipped on pallets. Liquid or low softening point resins are normally delivered in drums.

Depending on customer requirements, resins may also be delivered in molten form in tankers, dissolved in appropriate solvents, or in solid form in big-bags.

On storage in bags on pallets, resins, especially the lower softening point types, may undergo so-called cold flow, i.e., even at ambient temperature the resin particles tend to flow out of shape and stick together with the formation of bigger lumps, or even a solid mass, depending on pellet shape and size. Pressure and elevated temperature enhance these phenomena.

Some resin manufacturers also offer ready-made hydrocarbon resin dispersions of anionic, cationic, or nonionic type. As the application areas are manifold, the special requirements call for a close cooperation between customer and manufacturer to adapt the dispersion formulation to the special needs.

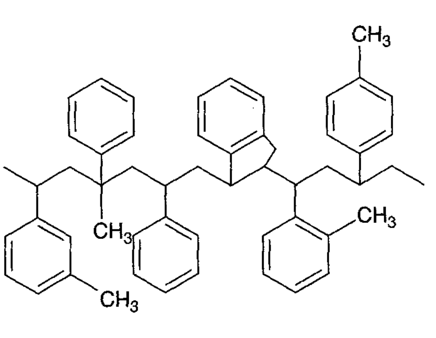
4 Resin Structure and Properties

4.1 Structure of Hydrocarbon Resins

As most hydrocarbon resins are produced from mixtures of monomers, containing small quantities of impurities which may interfere in the reaction, exact knowledge in resin structure is difficult to obtain. Little fundamental research is available on this type of material, but some basic information has been established.

4.1.1 Aromatic Resins

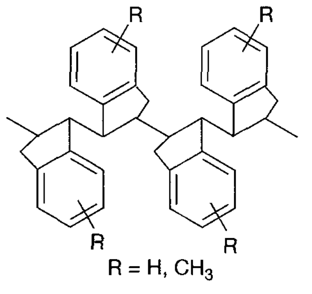
The main monomers are of the styrene and indene types. Thus, aromatic resin structure may be deduced from the atactic conformation of polystyrene. The indene structural elements introduce rigidity into the polymeric chain. Methyl groups on the aromatic ring (from vinytoluene) and in the polymer chain (from α-methylstyrene) increase steric hindrance to rotation. Coal-tar-based indene-coumarone resins and petrochemical-based C_9 resins differ only in the proportion of indene-type structures, which are present at higher concentration in indene-coumarone resins. A typical structural element of an aromatic resin is shown below:



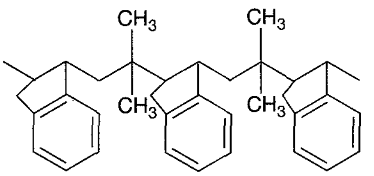
It should be mentioned that the original name "coumarone" resin is misleading insofar as the coumarone monomer is present only in very small quantities in the feedstock and the final resin.

Therefore, the tendency is to describe these resins as "polyindene" resins, but the term has never really caught on. The expressions coumarone resin or coumarone–indene resin, are still found in most official documents, e.g., custom laws and tariffs. This type of resin is referred to in this book as indene-coumarone resin.

Polyindene resins made from coal-tar fractions rich in indene and methylindenes, are highly rigid. The presence of methyl groups in the aromatic nucleus improves resin properties such as solubility and compatibility. The structural elements of a polyindene resin is shown below:

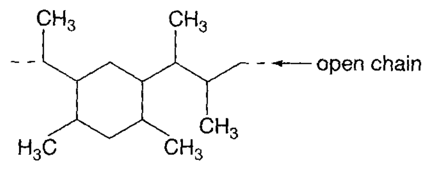


An aliphatic element may be introduced by copolymerization with aliphatic fractions (e.g., C_5/C_9 resins) or with aliphatic monomers, e.g., isobutene (e.g., C_4/C_9 resins). Thus, copolymerization of an indene–rich coal–tar fraction with isobutene, introduces aliphatic elements into the main chain, and reduces the polyindene-based rigidity, drastically altering the resin properties. Solubility and compatibility of such resins are improved, compared with polyindene resins. A possible structure is shown:



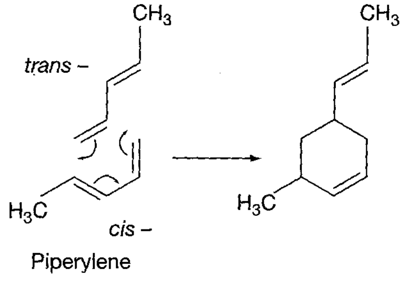
4.1.2 Aliphatic C_5 Resins

The structure of aliphatic resins is more difficult to determine, as feedstreams contain olefins and diolefins. They are not simply straight-chain polymers, but also contain cyclic structures, formed by internal cationic cyclizations. A possible structural element resulting from internal cyclization is shown:

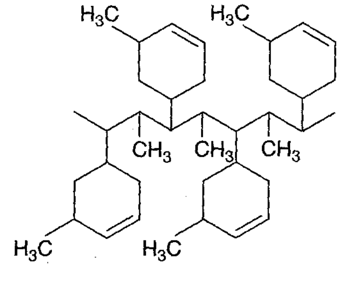


Resins made from piperylene concentrates show properties very close to terpene resins. The structures are supposed to be comparable with those of terpene resins, so they are sometimes called synthetic terpene resins.

The following mechanism has been suggested: In the first step, two piperylene molecules may dimerize by 1,4-addition to a cycloaliphatic monomer, which can then polymerize via the exocyclic double bond, as shown below:

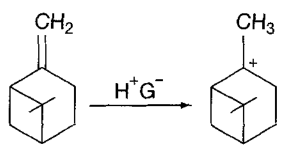


A possible structural element of piperylene resin is shown:



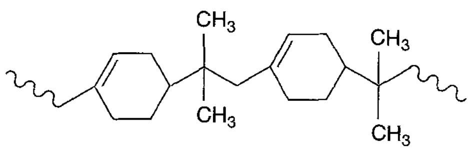
4.1.3 Polyterpene Resins

For the polymerization of β-pinene, the following mechanism has been suggsted by E.R. Ruckel [4.1] The first step (initiation) is formation of a carbocation in the presence of a Lewis acid ($H^+ G^-$).

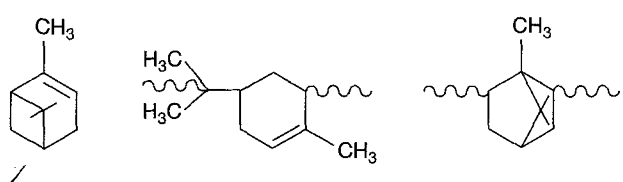


β-Pinene

Subsequent steps (propagation) are ring opening and subsequent polymerization, leading mainly to the structure represented below:



For resins made from α-pinene, the same author proposes the presence of two type units in a ratio of two (olefine type) to one (bicyclic type):

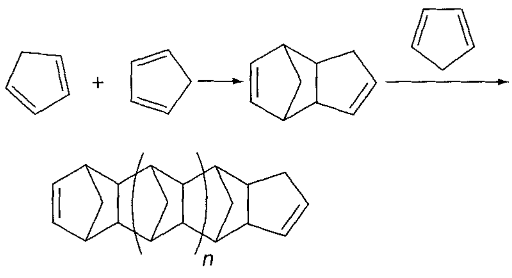


α ~~β~~-Pinene

The dipentene resin structure seems to be more complicated and is not yet fully elucidated. Different models have been reported (e.g., Ruckel) [4.2].

4.1.4 Dicyclopentadiene Resins

In contrast to the resins already mentioned, dicyclopentadiene resins are produced by thermal polymerization. Diels-Alder reaction and vinylic polymerization have been reported (M. Prillieux and A. Taketa) [4.3] [4.4]. The following reaction scheme is given:



4.2 Properties and Characterization

Knowledge of intrinsic properties of a resin may give useful information on its suitability for specific applications, and may also help to predict fundamental characteristics such as structure, aliphaticity or aromaticity, unsaturation, molecular mass and its distribution.

Table 4.1 Characterization Methods for Hydrocarbon Resins

Property	Method	Standard
Softening point	Ring and ball, °C Krämer-Sarnow, °C Mettler	ASTM D 3461-76, ISO 4625 DIN 53 180, NFT 67001 ASTM D 3461-76
Color	Gardner (50 % solution in toluene) Barrett (8 % solution in toluene)	ASTM D 1544-80(0-18), ISO 4630
	Saybold, Hazen, APHA (for low colors)	
Unsaturation	Bromine number, g Br_2/100 g	ASTM D 1159-84, DIN 51774, part 1
	Iodine number, g I_2/100 g	Wijs, ASTM D 1959-69
Acid number	mg KOH/g	DIN 51 558, DIN 53 402, ASTM D 974-80
Saponification number	mg KOH/g	DIN 51 559, DIN 53 401
Density	at 20 °C, g/cm^3	DIN 51 757
Flash point	°C, open cup (Cleveland)	ISO 2592

Resins are characterized by a number of properties. Commercial data sheets generally give the following items:

- Softening point
- Color
- Degree of unsaturation
- Acid number
- Saponification number
- Specific gravity
- Ash content

These properties are determined by standard methods (Table 4.1).

Other important properties such as solubility and compatibility, melt and solution viscosity, molecular mass and distribution, spectroscopic data (NMR, UV) are sometimes given in more specialized papers.

4.2.1 Hardness: Softening Point

The most popular criterion, reflecting the hardness and brittleness of resins, is the softening point. Other methods of measuring the hardness of a resin are needle penetration and glass transition temperature.

Indicative of the intrinsic viscosity, the softening point is controlled by the average molecular mass of the oligomeric material. In fact, softening of a resin occurs gradually over a range of temperatures, characteristic of noncrystalline amorphous material.

The softening point is defined as the temperature at which the resin flows under a given load on heating. Determination of the softening point has to follow a specified, closely defined method. General description of the standard methods - ring and ball (R & B), Krämer-Sarnow (KS), and Mettler softening point - are given below. Details can be found in the respective standards.

- Ring and ball Method (R & B): ASTM D 3461-76, DIN ISO 4625

This method is the most frequently used procedure for determining the softening point. The test equipment is shown in Fig. 4.1.

The resin is melted under well-determined conditions, poured into a metal ring of given proportions, and left to cool. A steel ball of given mass is placed on the ring. The temperature of the surrounding water or glycerol bath is raised at a predetermined rate. The temperature at which the ball forces the softening resin downward is noted as the softening point. In modern versions the test is carried out automatically (ASTM D 3461).

- Krämer-Sarnow Method (KS): DIN 53 180, NFT 67001

This is the oldest method and was initially used for tar pitches. The procedure is basically the same as the ring and ball method. Instead of a ring, a small glass tube open at both ends is used and the load is a small, measured quantity of mercury. The softening point is the temperature at which the mercury drop breaks through the softening resin and falls (Fig. 4.2).

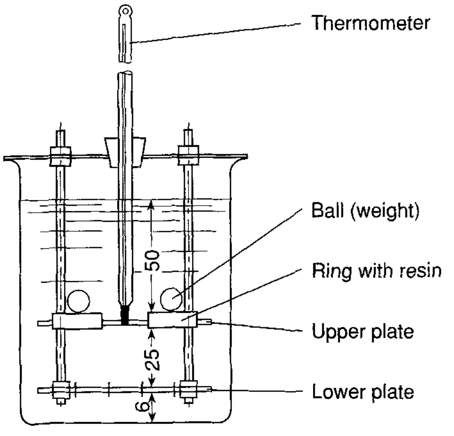


Figure 4.1 Determination of ring and ball softening point (numbers in mm)

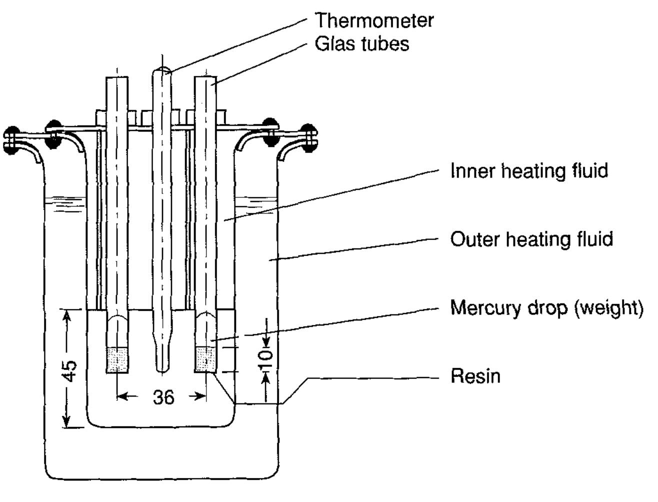


Figure 4.2 Determination of Krämer-Sarnow softening point (numbers in mm)

It is evident that the softening points obtained with these two methods are not identical. Figure 4.3 shows the conversion between them.

- Mettler Softening Point Method: ASTM D 3461-76

This more recent method automatically measures the temperature at which resin flows out of a standardized sample cup under its own weight. The temperature is recorded when the first drop crosses the light path of a photocell (Fig. 4.4) [4.5].

Although not widely used, some other measuring methods should be briefly mentioned: the capillary method, flow point, drop point, and the Kofler method.

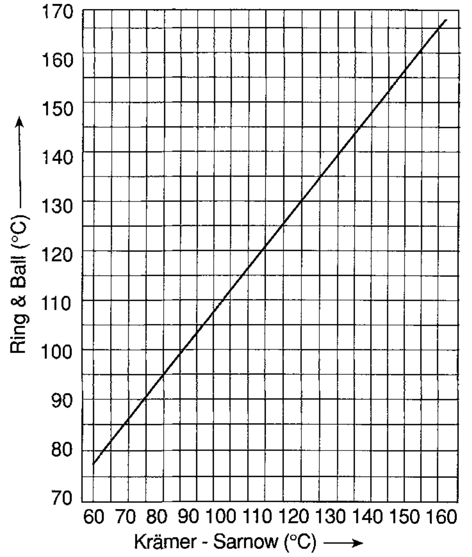
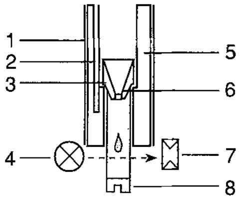


Figure 4.3 Conversion table Ring and Ball vs. Krämer-Sarnow



1 Heating element
2 Platinum resistance thermometer (Pt 100)
3 Sample
4 Light source
5 Furnace *7 Photo cell*
6 Sample cup *8 Collector sleeve*

Figure 4.4 Apparatus to determine the Mettler softening point

It is evident that the softening point of a resin is one of the most important criteria for resin choice in many end uses. Some examples are given:

Rubber-grade resins are mostly in the softening point range 70–100 °C R & B, resins for paints and lacquers in the range 100–120 °C R & B. Resins for many adhesive formulations, especially hot melts, have softening points of ca. 110–160 °C R & B.

It should be remembered that the softening points given in the manufacturer's specifications are always within a range of ± 5 °C, but most manufacturers supply the resins with a tolerance of only 3 °C.

Experience has shown that the effect of slight deviations from a defined softening point is different in the low, medium, and high melting range with regard to the specific end use. Thus, at the very low end (from liquid up to 80 °C R & B) a deviation of 5–10 °C in softening point may cause problems. In the medium range (80–100 °C R & B) a deviation of 15 °C and in the medium-high range (100–120 °C R & B) one of 10 °C is often tolerable. At the high end (130–170 °C R & B) a deviation of 3-5 °C is the maximum. The

reason is that in the low and very high softening point range the influence on the flow properties is particularly strong, and may lead to problems in the performance of the resin.

4.2.2 Color

Another important characteristic of hydrocarbon resins is color. Colors of commercially available resins range from water-white, through light yellow, yellow, yellow-brown, to dark brown, with the trend to light-colored or water-white resins. Manufacturers indicate resin color in their specification data.

The color can be determined by various methods, e.g., the Gardner, Barrett, Iodine color number or US Colophonium standard methods. Usually, resin color is indicated according to the Gardner or the Barrett standards. Table 4.2 shows the comparison between the four methods.

It should be pointed out that color not only varies in intensity, but may also differ in shade, going from yellowish to reddish to brownish.

Color is evaluated in resin solutions. A 50 % solution in toluene is used as the Gardner standard, a solution of 2 g resin in 25 ml toluene is the Barrett standard. These solutions, in calibrated tubes, are compared with a set of standard color disks. The comparison is carried out in commercially available comparators. (Fig. 4.5).

Table 4.2 Comparison of Color Standards for Resins

Barrett	Gardner	Iodine color number	US Colophonium standard
	6	10	X
	7	12	WW
1/2	8	15	WG
	8.5		N
	9	20	M
	10	25	K
1	11	40	I
	12	70	H
	12.5		G
	13	105	
1 1/2	14	145	F
	15	190	
	16	245	E
2	17	300	
2 1/2	18	445	D
3		2000	

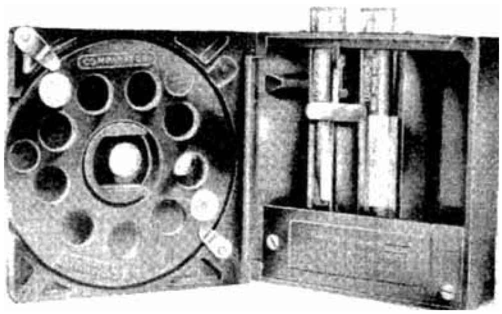


Figure 4.5 Color evaluation with a ***comparator***

Color may be an important factor in resin choice depending on end use. Pale colors are necessary in paints, lacquers, road markings, some types of adhesive, etc. Darker colors may be tolerated in rubber formulations, especially where carbon black filler is incorporated. Medium-colored resins can be used in most adhesive formulations, printing ink media etc.

In most applications, not only initial color but color change (discoloration) under the influence of light (W) and heat is important (see Section 4.2.12).

One has also to take into consideration the general trend to regard light-colored resins as pure, nonhazardous, while darker-colored resins are considered impure, hazardous, low-grade material. This is, of course, an absolutely unscientific point of view, which often leads buyers to select "over-engineered" resins without considering optimization of properties for the application envisaged.

It is also worth noticing that, in some very rare cases, a resin may show an unusual hue or tint or even fluorescence, giving the resin a very light but unexpected discoloration. The reason is often unknown. This does not affect the color grade measuring according to the Gardner or Barrett standards, but is nevertheless noticeable on optical inspection.

4.2.3 Unsaturation

Unsaturation is indicated by the bromine or iodine number, i.e., halogen addition to the double bonds, but in fact these numbers are not really specific for double bonds, as substitution reactions, especially at tertiary carbon atoms, may occur. Also, access to double bonds may be sterically hindered. Conversion of bromine number to iodine number and vice versa is not possible because of the different reactivity of bromine and iodine (I_2 less reactive than Br_2).

- Bromine Number: ASTM D 1159-84, DIN 51 774

Bromine acceptance is measured by an electrometric dead-stop method. The bromine number is defined as the amount of bromine in g accepted by 100 g of test material. This method can be used for minimum values of 0.5 g/100 g. Lower values are determined in accordance with DIN 51 774, part 2.

- Iodine Number: ASTM 1959-69, method Wijs

The iodine number is defined as the amount of iodine in grams accepted by 100 g of test material.

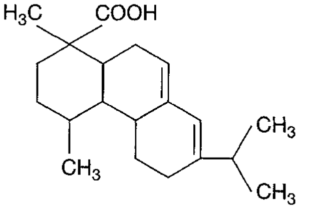
Approximate bromine number ranges of commercial resins are as follows (g Br_2/ 100 g):

- Nonreactive resins	ca. 10–45
- Reactive resins	ca. 55–75
- Highly reactive resins	ca. 65–100

The bromine or iodine number of a resin does not necessarily allow one to predict its reactivity, for instance with oxygen in the aging process. However, within a given resin series of approximately the same structure, relative comparison can be made, especially in the DCPD resin series.

4.2.4 Acid Number ASTM D 974-80, DIN 51 558, DIN 53 401

Resin data sheets always indicate acid and saponification numbers. These characteristics have been introduced as criteria for natural, colophonium-type resin (rosin) as rosin consists mainly (88-92 %) of rosin acids, mostly of abietic type.



Abietic Acid

The acid number is defined as the quantity of potassium hydroxide in milligrams required to neutralize 1 g of resin under fixed conditions.

Contrary to rosin or phenol-modified resins, unmodified standard hydrocarbon resins contain no functional groups, so in theory these resins have zero acid number.

Determination of acid number of hydrocarbon resins allows one to control deterioration by oxidation with formation of carbonyl and carboxyl groups. Especially for fine resin particles, a steady increase of the acid number is observed on prolonged storage.

Another reason for determining the acid number is the possible presence of residual catalyst traces. Typical acid numbers of different resin types are as follows (mg KOH/ g resin):

- Hydrocarbon resins	0.1
- Phenol-modified resins	0.3-0.5
- Maleic-modified resins	10–20 or higher
- Rosin	ca. 165

4.2.5 Saponification Number DIN 51 559, DIN 53 401

The saponification number is indicative of the presence of ester groups in a resin. As hydrocarbon resins do not contain any functional groups, their saponification number is normally zero, but is included in many resin data sheets by analogy to rosin and rosin derivatives (see Section 4.2.4). The saponification number is defined as the consumption of potassium hydroxide in mg by 1 g of resin under standardized conditions.

4.2.6 Density

Resin data sheets may list density or specific gravity. In fact, these may be regarded as identical, as the difference appears only in the fourth decimal place.

Density or specific mass is the mass of unit volume at a given temperature. Specific gravity is the weight of unit volume at a given temperature.

For solid resins, density is evaluated according to DIN 51 757 (or 52 004) at 20 °C or ASTM D-71 at 25 °C, for liquid or soft resins according to DIN 1995 U2, at 20 °C in g/cm^3 or ml. Comparison of density values allows one to make a rough classification of resins, as shown below:

– Aliphatic resins	piperylene-based	0.88–0.97
	C_5 olefin- and diolefin-based	0.93–0.97
	DCPD-based	ca. 1.1
– Terpene resins	α-pinene-based	0.90–0.98
	β-pinene-based	0.93–0.99
	D-limonene-based	0.99
– Aromatic resins	petroleum-based	1.06–1.11
	coal-tar-based	1.08–1.15

Some further characteristics of resins may be of interest to the user. They are

- Ash content
- Water content
- Other impurities
- Glass transition temperature
- Discoloration/yellowing
- Aging/oxidation.

4.2.7 Ash Content DIN 52 005

The usual reason that ash may be found in resins is the unwanted presence of inorganic impurities, owing to incorrect filtration of neutralization residues and rust contamination from storage tanks and pipelines. The presence of such inorganic impurities may contribute to premature aging, and may cause corrosion problems in paints. Normally, no ash is found in resins. Maximum values quoted are 0.1 %.

4.2.8 Water Content

It is self-evident that hydrocarbon resins do not usually contain water since they are hydrophobic materials, but water may be introduced by condensation during finishing operations or because of inappropriate storage conditions.

The water content of a resin is determined in accordance with DIN 51 777, part 1. This is the method used for mineral-oil hydrocarbons and solvents, i.e., the Karl Fischer direct method.

The presence of water may cause serious problems in several applications. For example, in resins used for hot-melt applications, water may lead to foaming. In resin solutions, the presence of water can result in opaque solutions.

Figures given in resin data sheets are generally $\leqslant$ 0.1 %, which is within the accuracy of measurement.

4.2.9 Residual Elements

The residual amounts of the other impurities in resins are not routinely controlled, as they are mostly zero or at any rate very small, and of no consequence for most purposes. Nonetheless, there are a few applications where the presence of particular elements may be important.

- Sulfur:

The sulfur content is significant when a resin is used as the starting material for making hydrogenated resins. The sulfur content of IC or C_9 hydrocarbon resins is commonly ca. 200–250 ppm. For hydrogenation purposes, it should be as low as 70–100 ppm, because of the ability of sulfur to act as a catalyst poison.

- Chlorine:

This is found in resins only where the traces of residual $AlCl_3$ have not been properly washed out after polymerization in C_5 resin manufacture.

- Fluorine and Boron:

As in the case of chlorine, very small quantities of fluorine and boron may be found, depending on the thoroughness of the process used to remove the catalyst residue from polymerization with BF_3 in the manufacture of IC or C_9 hydrocarbon resins.

Determination of these impurities was necessary when these resins were used in the formulation of chewing gum base. Maximum quantities permitted were 2 mg/kg for boron and 3 mg/kg for fluorine in the aqueous extract from chewing gum base. After many decades of use, IC and C_9 resins are no longer listed as approved by the FDA for use in chewing gum.

4.2.10 Glass Transition Temperature

Every amorphous polymer has a glass transition temperature T_g, resulting from the reduction of molecular mobility by the collapse of free volume with falling temperature.

Glass transition temperature may be measured according to DIN 57 015 or by differential scanning calorimetry (DSC) [4.6]

Hydrocarbon resins normally have high transition temperatures. Depending roughly on the softening point, T_g of resins is about 30–85 (R & B 85–140 °C), in comparison with T_g of natural rubber of ca. −68 °C. Therefore, hydrocarbon resins can be used to raise the average T_g of a polymer, for instance, in rubber or adhesive formulations.

T_g measurements also allow one to determine the compatibility of blends: compatible resin–polymer blends exhibit only one T_g, whereas incompatible blends show a second glass transition temperature.

4.2.11 Thermal Stability

Thermal stability of resins is of importance in all types of compounding and applications where heat is applied, for example, in hot-melts (mixing, compounding, and application), hot-applied road marking plastics, jointing, sealants, bituminous roofing compounds, and similar applications.

On application of heat, resin degradation may result in color change, viscosity change, skinning, gel formation, evolution of odor, etc. It may also influence the properties of the formulated product, for example, deterioration of tack and peel strength, or flexibility. Oxidation and depolymerization may also occur.

There is no standard method to evaluate thermal stability; it depends on the specific requirements of special areas of application.

With regard to chemical nature, it is usually assumed that aromatic resins with high indene content (IC resins) are less stable than resins with high styrenes content (C_9 resins). Stabilized resins, containing antioxidants, are available. Stabilized indene–coumarone resins show a remarkably improved thermal stability coming close to that of C_9 resins with a high content of styrenes.

Usually, consumers of resins for application involving exposure to heat add antioxidants to the formulations.

4.2.12 Discoloration/Yellowing

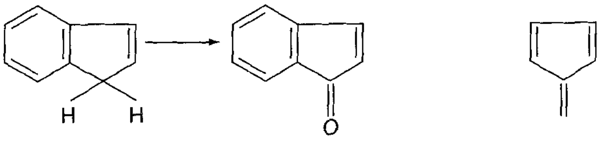
Color stability is important in all cases where resin-containing formulations are exposed to light and oxygen, e.g., light-colored paints, lacquers, coatings, white road markings. Other applications where discoloration may be a problem are floor tiles, some types of adhesives, non-woven materials, etc.

Aliphatic resins and pure aromatic resins are less sensitive to this phenomenon than aromatic resins manufactured from petroleum or coal-tar-based feedstreams.

However, it has to be noted that discoloration normally does not affect intrinsic resin properties, so that in all applications where color is not a problem, the tendency for a resin to discolor has no adverse consequences.

The following explanation for discoloration has been offered: After the polymerization process, some double bonds still remain, mostly in terminal positions, and these are responsible for discoloration, and to some degree for aging.

A possible theory is that this phenomenon is linked with the 5-ring in the indene molecule, with its very reactive methylene group, which, under the influence of light and atmospheric oxygen changes to a fulvene structure. This is pictured in a simplified, hypothetical reaction scheme:



Indene Fulvene structure (chromophor)

The cause of yellowing, as far as the theory is concerned, is that all fulvenes are intensely yellow, yellow-orange, or yellow-brown in color, so that the presence of even small quantities of this type of structure may lead to visible effects.

The reason is that conjugated, chromophore structures are characteristic of fulvenes. They easily undergo autoxidation and polymerization. Simply shaking a solution with air will lead to formation of peroxides as a first stage for further oxidation.

4.2.13 Aging and Stabilization

Like all polymers, resins undergo aging phenomena under the influence of oxygen, heat, and light. Typical results of these influences are deterioration of the outward appearance, for instance yellowing, loss of gloss and transparency, and general deterioration of physical and mechanical properties.

It is of great interest to minimize these effects. This is usually achieved by special additives such as antioxidants and/or light stabilizers.

4.2.13.1 Antioxidants

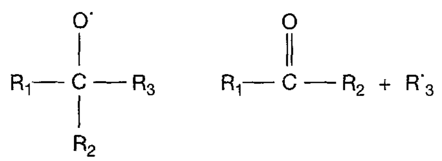
Antioxidants are chemical substances with retarding effects on oxidation, and thus on the resulting aging problems. Very small quantities, < 1 %, are often sufficient and should be added at the earliest possible stage (production and/or compounding).

Oxidative attack can be explained as a series of radical chain mechanisms represented by the simplified scheme below:

Initiation	$RH \rightarrow R^{\cdot}$
Propagation	$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$ $ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$
Branching	$ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH$
Termination	$2\,R^{\cdot} \rightarrow R\text{-}R$ $R^{\cdot} + ROO^{\cdot} \rightarrow ROOR$ $2\,ROO^{\cdot} \rightarrow$ inactive products $+ O_2$

Recombination of polymer radicals may lead to crosslinking.

Another reaction type may result in chain scission:

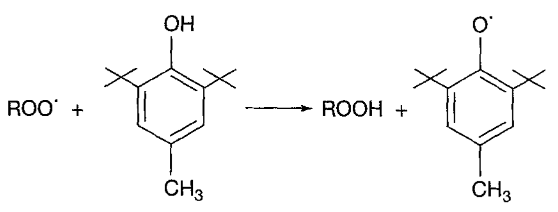


At higher temperatures (> 150 °C) the monomolecular decomposition of hydroperoxides may lead to branching. The generated radicals $RO^{\cdot}$ and ${}^{\cdot}OH$ may react with RH as shown, with formation of alcohols and water:

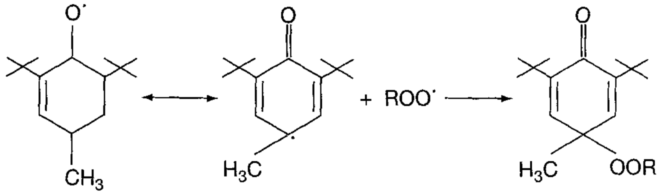
$$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$$
$${}^{\cdot}OH + RH \rightarrow H_2O + R^{\cdot}$$

The role of antioxidants is to prevent the initial step-formation of the first radical. Two types of antioxidants may be distinguished: primary antioxidants (chain propagating inhibition) and secondary antioxidants or synergists (peroxide decomposition).

Primary antioxidants are mainly sterically hindered phenols such as 2,6-di-*tert.*-butyl-p-cresol (BHT) or secondary aromatic amines. Reaction follows the scheme:



The chain reaction is inhibited; only one ROOH is formed.



No ROOH is formed.

Secondary antioxidants (costabilizers or synergists) are usually phosphites or thioesters. In conjunction with primary antioxidants, they function by decomposing hydroperoxides, which could otherwise form radicals:

$$ROOH + P\,(OR')_3 \rightarrow ROH + O{=}P(OR')_3$$
(phosphite)
$$ROOH + R'\text{-}S\text{-}R' \rightarrow ROH + R'\text{-}S\text{-}R'$$
(thioester)

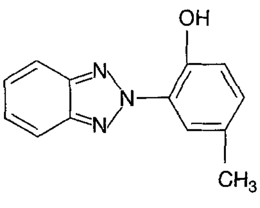
Antioxidants with more than one phenolic group in the molecule, and many other substances with similar structural characteristics, show a further improved effectiveness as compared with standard BHT. It should be mentioned that, in many applications, a combination of both types of antioxidants is used, for example in the hot-melt industry.

4.2.13.2 Light Stabilizers

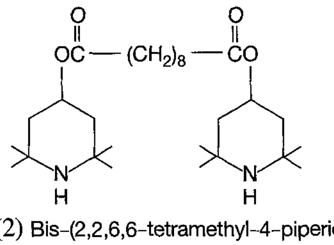
Light stabilizers are chemical substances which can interfere in the physical and chemical processes of light-induced decomposition of polymers.

UV absorbants and quenching agents act predominantly physically, whereas hydroperoxide-destroying agents and radical-capturing agents act chemically. They are consumed during aging.

Light stabilizers normally used for resins are of the benzotriazole type (1) which act by UV absorption and sterically hindered amines (2) which act by radical capture.

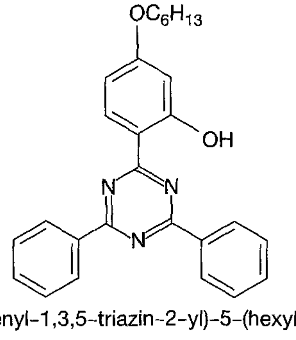


(1) 2-(2'-Hydroxy-5'-methylphenyl)benzotriazole



(2) Bis-(2,2,6,6-tetramethyl-4-piperidyl)sebacate

Less volatile UV absorbers are also available, e.g.:



2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxyphenol

Various commercial resins containing stabilizers are available. Polyterpene resins, which are very sensitive to oxidation, always contain stabilizers. Stabilized aliphatic resins are also available. Aromatic resins, especially those with a very low indene content, normally need no stabilization. However, for special applications stabilized types are available commercially.

4.2.13.3 Shelf-Life

Resin samples are packed in small plastic bags or more commonly in small plastic bottles. Although the bulk of the sample consists of resin chips or pastilles, there is always a limited amount of finer resin particles or dust. It is therefore unavoidable that, when a small sample is being taken from the bottle for testing, the fines are taken for analysis instead of bigger chips or pastilles, just to avoid having to grind or pulverize the sample before testing.

All resins are subject to aging, i.e., oxidative attack, which has a greater effect on the smaller resin particles. Consequently there is the risk that fines taken from the bottle for testing have already been exposed to a premature aging process with the result, that the analysis may not be typical of the bulk material.

It should be noted, however, that even the bulk of the sample may already have undergone aging, depending on the time of storage, and the exposure to air and sunlight, which accelerate aging.

As result of that aging process some of the physical data of the resin may have changed to show:

- Increased acid number
- Premature color degradation (discoloration, yellowing)
- Reduced solubility and compatibility (higher cloud point; see Section 4.3.4.1).

The limited shelf life of resin samples is easily demonstrated by comparing the analytical data of a pulverized resin sample held in a flat, open tray and exposed to air and sunlight, with the assay of a lump sample taken from a sample bottle which has been kept closed and protected against sunlight.

It follows that, in selecting a particular resin on the basis of preliminary tests with a sample, the limited shelf-life should always be taken into account. To be on the safe side, one should use fresh samples, where premature aging due to prolonged storage is not to be expected.

4.2.14 Solubility

Generally, hydrocarbon resins are soluble in most common organic solvents, especially aromatics, esters, ethers, and chlorinated solvents. They are insoluble in water, alkalis and mineral acids. Solubility depends on resin type, its average molecular mass and distribution. Higher softening point resins are less soluble than lower softening point types. Aliphatic resins exhibit better solubility in aliphatic solvents. Aromatic resins are soluble in acetone.

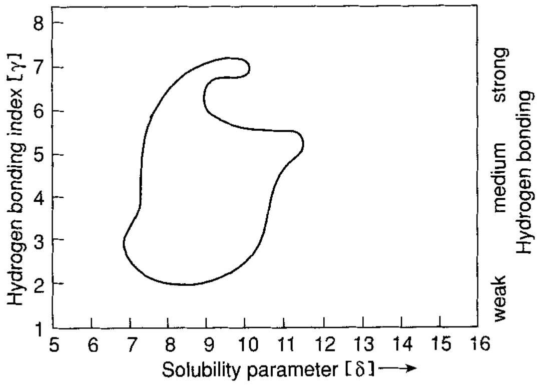


Figure 4.6 Solubility contours of indene-coumarone resins

To dissolve a resin requires a similarity of attractive forces between the resin and the solvent compared with the attractive interaction between individual resin molecules and individual solvent molecules (like dissolves like).

A system of predicting solubility has evolved on the basis of the forces required to separate molecules, as when a liquid is vaporized. With solvents of varying solubility parameters and hydrogen bonding indices, it is possible to determine the solubility parameter of a resin. On this basis, when two materials have very similar solubility parameter data, they should also be compatible.

In drawing up of a solubility diagram, the hydrogen bonding index and the solubility parameters of various solvents are important. Aromatic, aliphatic, chlorinated, and hydrogenated hydrocarbons show weak hydrogen bonding; esters, ethers, and ketones have medium, and alcohols, glycols, and amines have strong hydrogen bonding.

The diagram is drawn up by plotting the hydrogen bonding index γ of the solvent as ordinate and the solubility parameter δ as abscissa, all data referring to a defined resin.

For a defined resin, all possible solvents will be within the closed curve produced by this plot; the unsuitable solvents are outside this area. A solution diagram summarizing the single diagrams of indene-coumarone resins with a softening point range 60–140 °C R & B is shown merely as a general example in Figure 4.6.

Solvents with data combinations (γ and δ) very close to the border of the curve may give opaque solutions. In borderline cases, the attractive forces between the resin molecules are so strong that the aggregates formed show a high viscosity. Should a solvent be selected from the middle area of the diagram, the formation of bigger aggregates is avoided, resulting in a low viscosity.

4.2.14.1 Cloud Point

Solubility of resins is mostly evaluated by determination of the cloud point, less commonly by the aniline and mixed aniline point [4.7].

The cloud point measures the solubility/compatibility of a resin with solvents. The value reported is the temperature at which a specific mixture of a resin and a solvent gives a cloudy appearance, having been cooled from a temperature at which the mixture was clear.

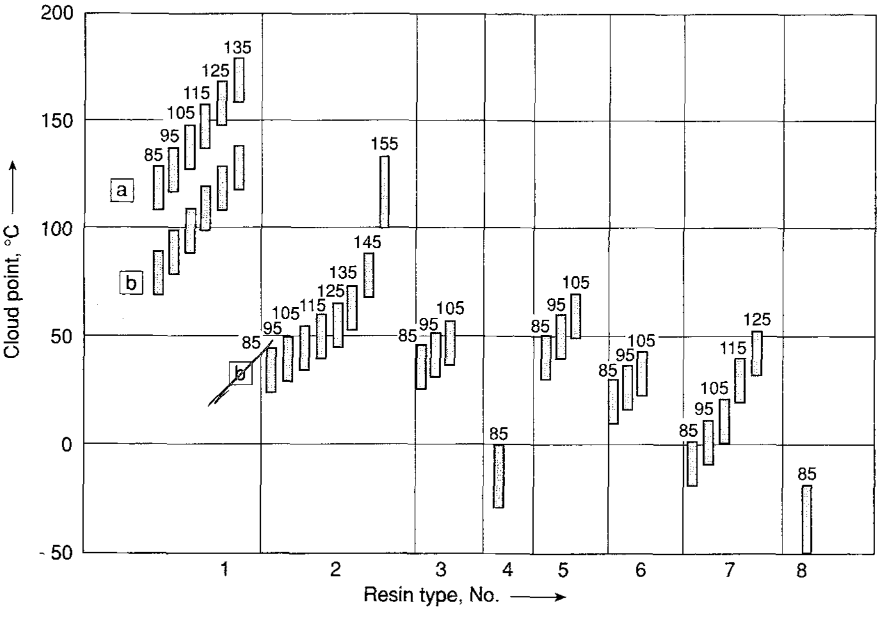


Figure 4.7 Cloud points of indene-coumarone and C_9 hydrocarbon resins. The values refer to the softening point according to Krämer-Sarnow
50 % solution in isoparaffin oil (free of aromatics)

Resin types:

1) Indene-coumarone, (a) nonisothermal, (b) isothermal polymerized; 2) C_9 resin, special cut; 3) C_9 resin, special cut; 4) C_9 resin special cut, C_4-modified; 5) C_9 resin, special cut, phenol-modified; 6) C_9 resin, special cut, C_4-modified; 7) C_9 resin, special cut, C_4-modified; 8) C_9 resin, standard, C_4-modified

This cloudy appearance does not come instantly, so it is necessary to define the test conditions exactly. Commonly, a test tube of a given diameter is used. The temperature is noted when the lower end of the thermometer, held on the far side of the tube, disappears.

It is better to replace the somewhat subjective method with an objective measuring principle, e.g., a multipurpose apparatus with constant heating or cooling rate, measuring and recording the optical transmittance (e.g., the Mettler FP 800 Thermosystem or similar adapted apparatus). Resins with cloud points below 0 °C are commonly regarded as soluble.

White spirit with various aromatic contents is a widely used solvent in the determination of the cloud point, but other solvents are also used. Figure 4.7 shows the cloud points of various resin types with different softening points. The solvent used is an isoparaffinic oil free of aromatics [4.8].

4.2.14.2 Aniline and Mixed Aniline Point

The aniline point test is much the same as the cloud point test, but the solvent is aniline, a very polar material. It is measured in accordance with DIN 51 775 (modified). The aniline

point is defined as the temperature at which a mixture of equal parts of aniline and the test substance show the beginning of phase separation, i.e., the onset of clouding (Section 4.2.14.1). The aniline point allows one to draw conclusions about the composition of the test substance. For instance, phase separation (cloud point) for aromatic resins occurs between +15 °C and below zero; for resins with intermediate aromaticity, it lies between 30 °C and 50 °C; and for nonaromatic resins it is 50 °C to 100 °C (and over).

These are only approximate figures, as the aniline point also depends on the specific molecule (molecular mass).

Sometimes the mixed aniline point is used. It is defined as the temperature at which a homogenous mixture of one part each of the resin sample and aniline, plus one part of *n*-heptane, shows phase separation on cooling. One inherent deficiency of both types of cloud point tests is that small amounts of high molecular mass material, or highly paraffinic components in some solvents, tend to precipitate first and obscure the chemical differences one is trying to observe.

4.2.15 Compatibility

Generally, hydrocarbon resins are compatible with a large number of materials, such as drying oils, plastisizers, polystyrene, polyethylene waxes, rubber, and other elastomerics.

Clear definition of compatibility is rather difficult. Normally, it is understood as a clear transparent mixture of a resin with a given polymer. But in fact, the phenomenon is much more complex, and may be further evaluated by study of specific physical properties, such as glass transition temperature. A compatible blend is defined as having only one glass transition temperature, whereas blends with two or more transition points are considered incompatible.

Compatibility depends on resin type, molecular mass and its distribution, resin structure and configuration, and finally on application requirements. In some applications, full compatibility is sometimes undesirable.

The most commonly used method of measuring compatibility of a resin with other substances is to dissolve both materials in a mutually compatible solvent, and to cast a film on a glass slide. After solvent evaporation a compatible system gives a clear film while incompatibility results in an opaque film. A further refinement is to examine the film with a phase microscope. Instead of dissolving, the components may be melted together. Compatibility or incompatibility is observed on the film after cooling. It should be noted, however, that this does not always serve to explain observed differences, as for instance in rubber compounding. Nevertheless, it is widely accepted as a useful and easy method.

Normally, the end user will select a fully compatible resin for obvious reasons, regardless of the area of application. However, there are many applications where borderline compatibility is tolerated or even desirable. A few examples are mentioned to illustrate this.

Certain C_9 hydrocarbon resins, depending on type, may exhibit borderline compatibility in combination with short-oil alkyds. This will show as an opaque film in the compatibility test outlined above.

In a clear alkyd-based lacquer this would be prohibitive. On the other hand, if the formulation provides for a pigmentation, an opaque film in the test can most likely be tolerated, as a slight haziness of the resin/alkyd blend will be obscured by the pigment.

A second example is taken from the adhesive industry. Straight indene-coumarone resins would in principle be excellent tackifiers in formulating hot-melts in combination with ethylene-vinylacetate (EVA) copolymers. However, IC resins have relatively poor compatibility with EVA copolymers. Nonetheless, IC resins have indeed been used, provided that the blend does not show actual separation into two distinct layers.

As a matter of fact, there are more reports from the adhesive industry, that borderline compatibility or controlled incompatibility may even lead to enhanced tack. A slight incompatibility can also be tolerated in filled hot-melts, for instance edge veneer hot-melts, but not in unfilled systems, mostly for purely visual rather than for technical reasons.

On the other hand, borderline compatibility is not always acceptable. A resin with borderline compatibility is used in combination with an oil or plastisizer in formulating a binder for a given substrate. A slight incompatibility may lead to a more pronounced phase separation, showing in the oil or plastisizer migrating to the surface of the substrate, possibly causing an oily, tacky surface.

Although complete compatibility is generally desirable, it can be stated from experience that many application areas exist where borderline compatibility can be of specific technical advantage. A consequence of this is that many resin manufacturers, having the capability to adjust the chemical composition of their resins to the requirements of their customers, may choose to include less compatible resin constituents in the specially adjusted, final resin.

4.2.16 Viscosity

Solution or melt viscosity (flow properties/rheology) are very important physical properties, and may be significant in many applications, for example in adhesives, paints and coatings, printing inks, and blends with various polymers.

4.2.16.1 Solution Viscosity

Various physical and chemical factors can influence solvent viscosity; the most important are:

- Concentration
- Softening point/molecular mass
- Molecular mass distribution
- Chemical composition of the resin
- Type of solvent

It is self-evident, that solution viscosity is a function of resin concentration: the higher the resin concentration the higher the viscosity. For a given concentration, solution viscosity depends to a first approximation on the resin softening point, as illustrated in Figure 4.8.

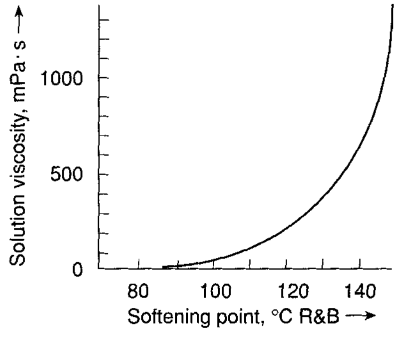


Figure 4.8 Solution viscosity as a function of softening point. Aromatic C_9 resin, 50 % in white spirit with 5 % aromatics

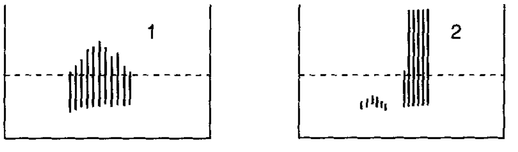


Figure 4.9 Molecular mass distribution (schematic)
1 Straight resin 2 Fluxed resin

This is true for given resin types produced under similar conditions. As in this case the softening point is a function of the average molecular mass, it is evident that solution viscosity depends on both softening point and average molecular mass.

Molecular mass distribution (see also Section 4.2.17) also has an important effect on viscosity. This can be explained by the following idealized example, which has nevertheless been corroborated by experience.

Two resins with the same softening point are considered (Fig. 4.9). Resin 1, produced by a straight process, has a normal molecular mass distribution. Resin 2, produced in the same general way, but with a higher softening point, has been blended (fluxed) with liquid oligomers to adjust (reduce) the softening point, and thus has a totally different distribution curve.

As the broken line demonstrates, the average molecular mass is the same for both resins. However, comparison of the solution viscosity of both resins in a given solvent shows that it is higher for resin 2, approaching the viscosity of the higher molecular mass portion of resin 2 (i.e., the original, oligomer-free resin).

Resin structure also affects solution viscosity. A solution of an aromatic resin in an aromatic solvent has a lower viscosity than that of an aliphatic resin; a solution of an aromatic resin in an aliphatic solvent shows a higher viscosity than that of an aliphatic resin (and vice versa). This is related to the chemical affinity between resin and solvent, and thus to solubility. This is illustrated in Table 4.3 [4.9].

Table 4.3 Resin solution viscosities (70 % solution at 25 °C)

Solvent	Viscosity, P	
	Indene-coumarone resin (100 °C R & B)	C_5 petroleum-based resin (100 °C R & B)
Toluene	4	8
Mineral spirit	40	22

The highest viscosities are obtained when resin solubility in a given solvent approaches the borderline.

4.2.16.2 Melt Viscosity

Melt viscosity is of great importance, especially in hot-melt adhesives. Another area where melt viscosity plays an important role is in rubber compounding, where modifying resins are used as tackifiers, together with selected oils. They are also used as viscosity regulators, to facilitate mixing (processing aid).

The major points influencing melt viscosity are the following:

- Softening point
- Average molecular mass
- Molecular mass distribution
- Resin type

For a given type of resin, viscosity is a function of the softening point. This is demonstrated in Figure 4.10. It can bee seen that the melt viscosity for resins ranging from medium to relatively high softening points, ca. 90–120 °C R & B, does not vary dramatically. In the higher softening point range, ca. 130 °C R & B and higher, a small increase in the softening point will produce a steep viscosity increase.

This may be very important in some special applications, for example in some hot-melt adhesive formulations. Resins used for such applications tolerate only 2–3 °C deviation

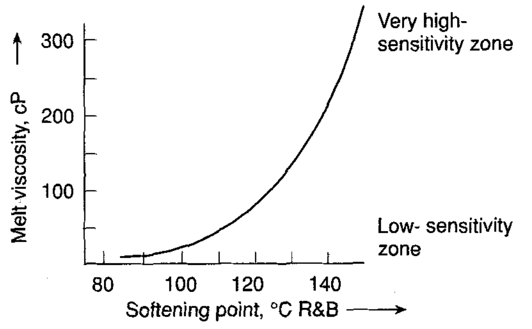


Figure 4.10 Melt viscosity as a function of softening point

Table 4.4 Melt viscosity and molecular mass of petroleum-based hydrocarbon resins

	C_9 (112 °C R & B)	C_5 (115 °C R & B)
Viscosity, cP		
300 °F (149 °C)	4500	22000
350 °F (177 °C)	475	1800
400 °F (204 °C)	95	315
Molecular mass		
M_w	875	2150
M_n	575	1000
M_w/M_n	1.5	2.2

from the given standard, otherwise severe handling problems on the hot-melt coating machine may result.

Comparing resins of different type, e.g., aliphatic and aromatic, with the same softening point, it appears that viscosity is influenced mostly by molecular mass, as illustrated in Table 4.4.

Typical melt viscosities of indene-coumarone and C_9 hydrocarbon resins are shown in Figures 4.11 and 4.12. Figure 4.13 shows the average molecular mass of IC and C_9 resins.

From what is known of the chemical structure of the two resins, a C_5 resin has more opportunities for bond rotation, and greater chain flexibility compared with the more rigid

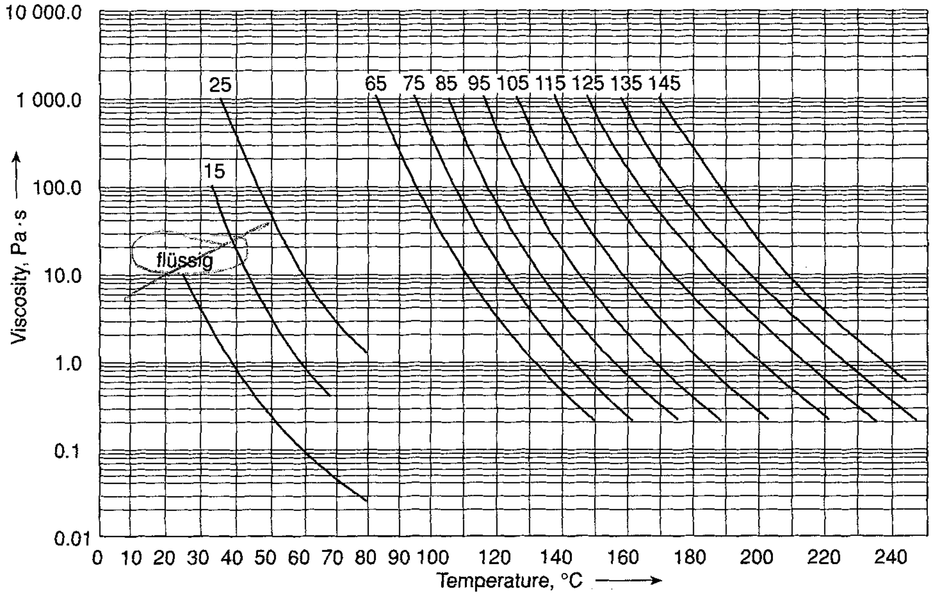


Figure 4.11 Melt viscosity of indene-coumarone resins of different softening points (Krämer-Sarnow)

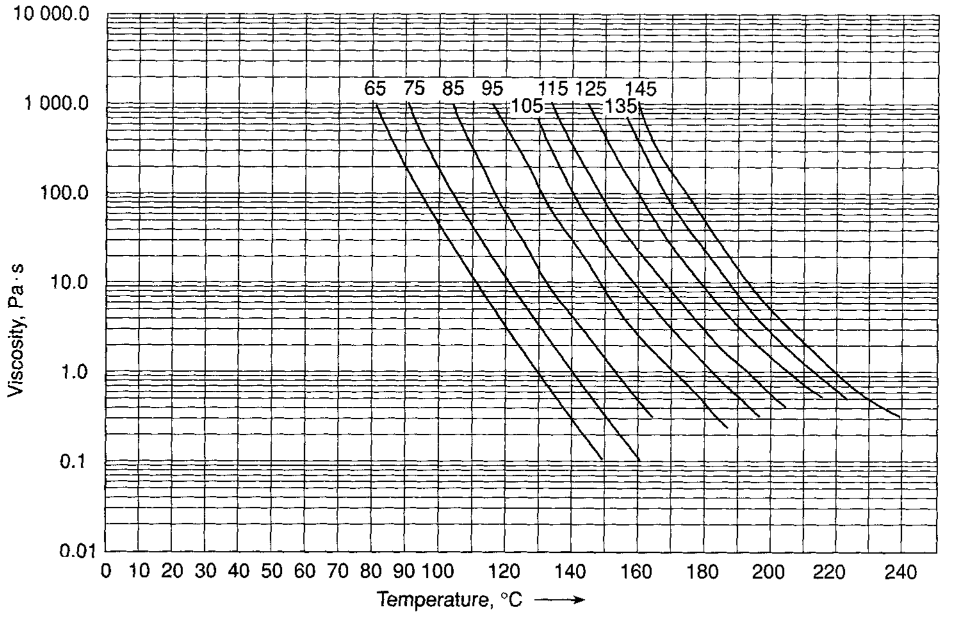


Figure 4.12 Melt viscosity of C_9 hydrocarbon resins of different softening points (Krämer-Sarnow)

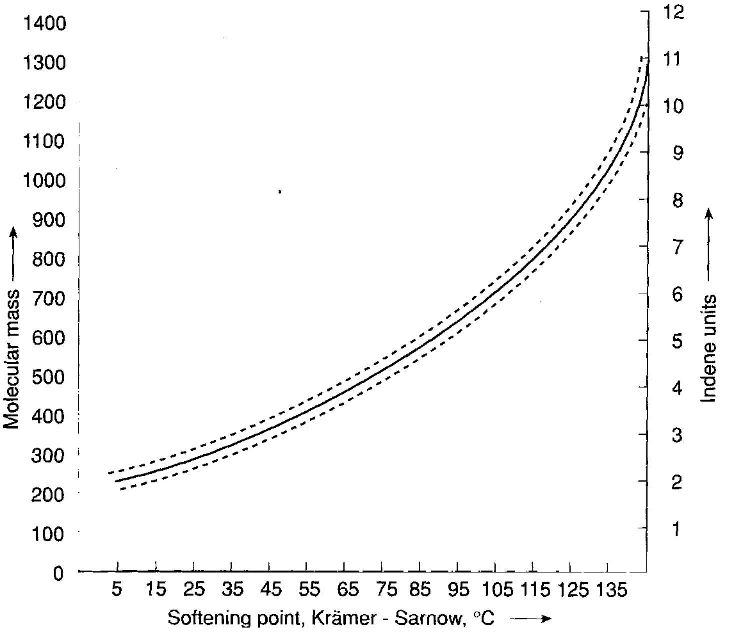


Figure 4.13 Average molecular mass of indene-coumarone and C_9 resins

structure of the indene-coumarone resin molecule. It is for this reason that a higher molecular mass is required for a C_5 resin to achieve a softening point of 100 °C R & B [4.10].

To summarize, the C_5 resin shows a higher melt viscosity, despite its higher flexibility, because of the higher molecular mass, i.e., the molecular mass is more important than the chemical structure.

Another important influence on melt viscosity is the molecular mass distribution. A definite softening point or average molecular mass may be obtained in a number of different ways:

- by adjusting polymerization conditions
- by addition of oligomers or oils to a resin of higher softening point
- by elimination of oligomers from a resin of lower molecular mass

It is evident that the molecular mass distribution may be totally different, thus influencing the melt viscosity. Low molecular mass oligomers act as a solvent, thus lowering the viscosity, whereas the absence of low molecular mass oligomers leads to higher melt viscosities.

4.2.17 Molecular Mass and Molecular Mass Distribution

Resins, in common with all polymeric materials, are mixtures of distinct molecules of different size. Molecular mass measurements give the average of molecular masses. For a specified resin type, the softening point (or glass transition temperature) is a function of the average molecular mass.

Depending on the resin type (C_5, C_9, or cycloaliphatic) the average molecular mass may differ widely, owing to a more or less rigid molecular structure, as illustrated in Table 4.5, together with the data for terpene resins.

Table 4.5 Average molecular mass of resins

Resin type	Softening point, °C R & B	$\overline{M}_n$
Indene-coumarone	100	700*
C_5	100	1200*
β-Pinene	115	1030**
Dipentene	115	720**
α-Pinene	115	815**

* By freezing point depression [4.11] ** By vapor pressure osmometry [4.12]

It follows from these data that dipentene resin has a lower molecular mass than β-pinene resin for a specified softening point, indicating a more rigid and compact structure than β-pinene resin, which has a more extended and flexible chain.

The molecular mass distribution (MWD) $\overline{M}_w/\overline{M}_n$ gives an indication of the polydispersity of a resin. An illustration for two resins is given in the idealized example shown in Figure 4.14.

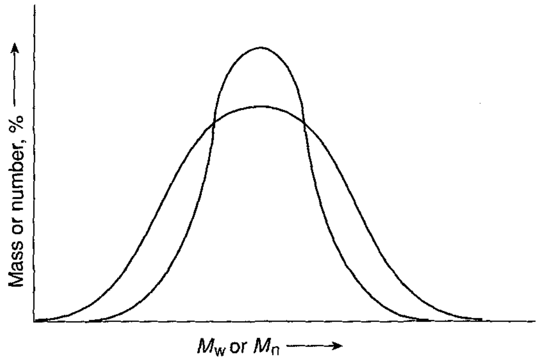


Figure 4.14 Molecular mass distribution of two resins

Thus, resins having the same softening point may differ widely in molecular mass distribution. An example illustrating the influence of this difference is given in Table 4.6.

Table 4.6 Molecular mass and properties of two aliphatic petroleum-based resins with softening point 100 °C R & B

	Resin 1	Resin 2
M_w	2500	1500
M_n	1000	900
M_w/M_n	2.5	1.7
Melt viscosity, cP (300 °F)	3900	3000
Cloud point (in a given mixture)	155	120

Typical molecular mass data for commercial C_9-based resins from different producers are given in Figures 4.15 and 4.16.

The mass distribution for a special cycloaliphatic resin (softening point 91 °C R & B, $\overline{M}_w$ 1153, $\overline{M}_n$ 851, $\overline{M}_w/\overline{M}_n$ 1.35) is given in Figure 4.17.

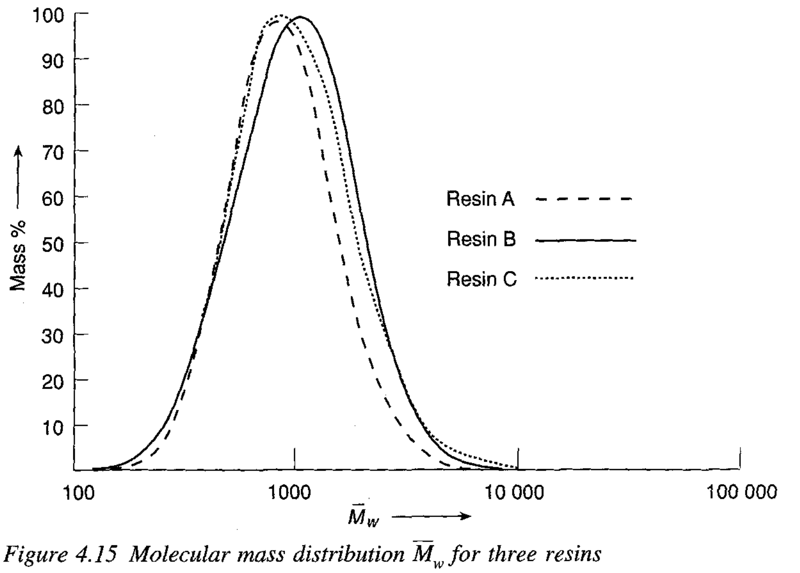


Figure 4.15 Molecular mass distribution $\overline{M}_w$ for three resins

Data for the three resins are as follows:

	Softening point, °C R & B	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
Resin A	*97*	*1030*	*728*	*1.41*
Resin B	*100*	*1190*	*802*	*1.48*
Resin C	*100*	*1152*	*756*	*1.52*

The MWD figure shows a homogenous distribution of molecular mass.

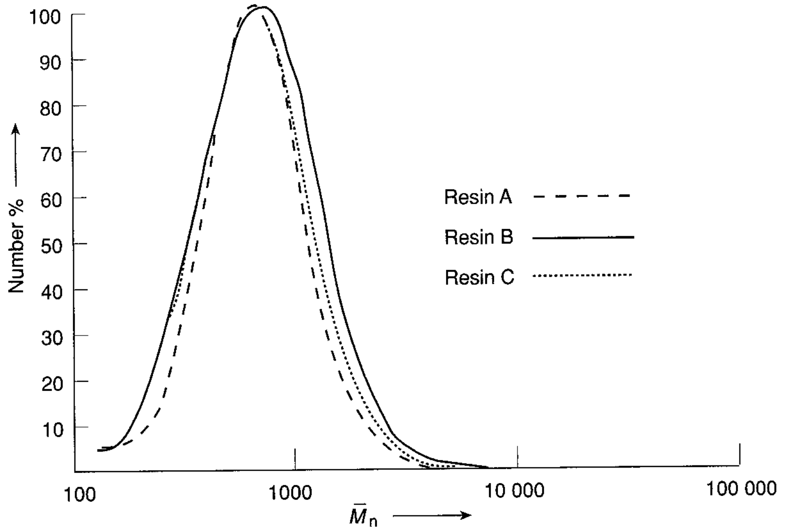


Figure 4.16 Molecular mass distribution $\overline{M}_n$ for the same three resins as in Figure 4.15

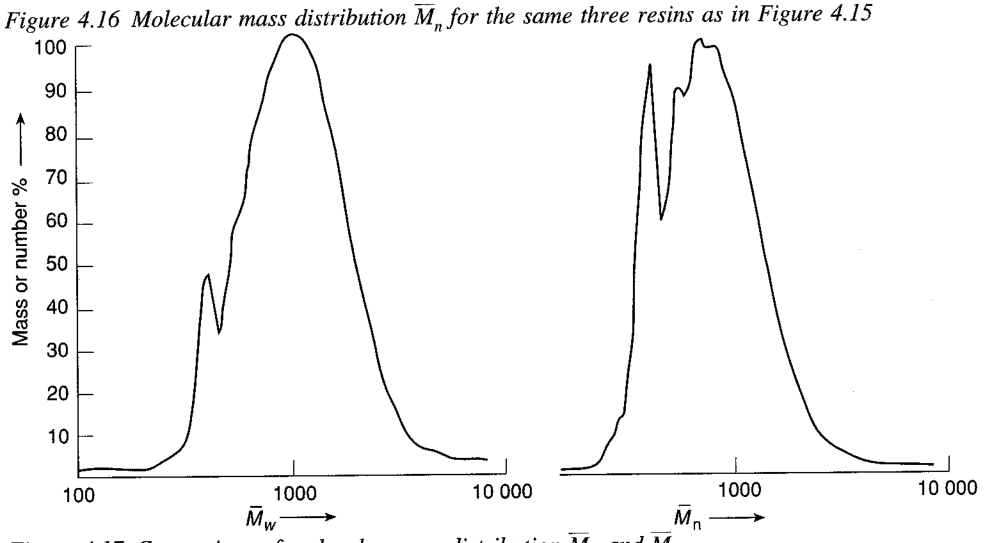


Figure 4.17 Comparison of molecular mass distribution $\overline{M}_w$ and $\overline{M}_n$

The graphs clearly show a discontinuity in the molecular mass distribution, indicating an unusual contribution of lower molecular mass species, added to the initial resin to adjust properties or formed in the manufacturing process, possibly by undesired cracking.

The most usual method for determination of molecular mass is gel permeation chromatography (DIN 55 672).

4.2.18 Spectroscopic Data

Commonly employed spectroscopic methods to characterize resins are:

- Infrared (IR)
- Ultraviolet (UV)
- Nuclear magnetic resonance (NMR-H/NMR-C)

4.2.18.1 Infrared Spectroscopy

The main object of IR analysis is the detection of chemical functional groups. In the first instance it allows one to distinguish neutral and functionalized resins, from the presence of COOH, OH, or other functional groups. Typical absorption bands of functional groups occur in the region above 1500 cm^{-1}. This is illustrated by the spectrum of rosin (Fig. 4.18) [4.13].

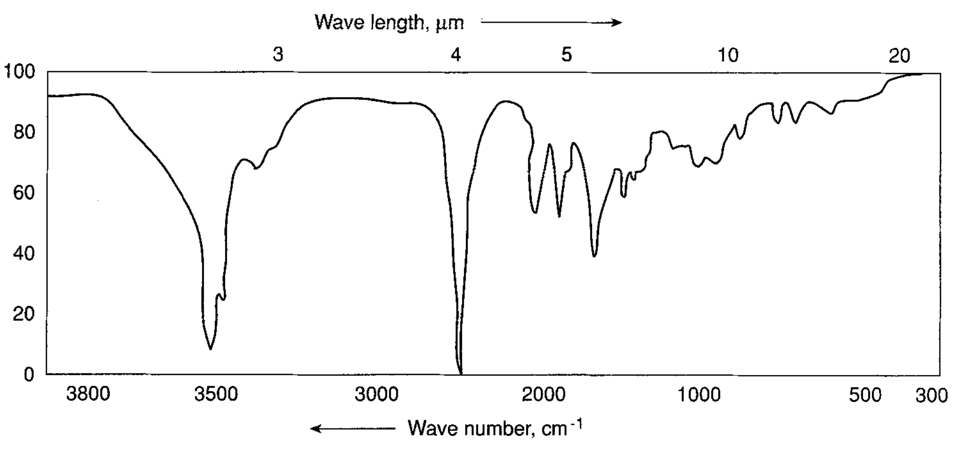


Figure 4.18 Infrared absorption spectrum of rosin

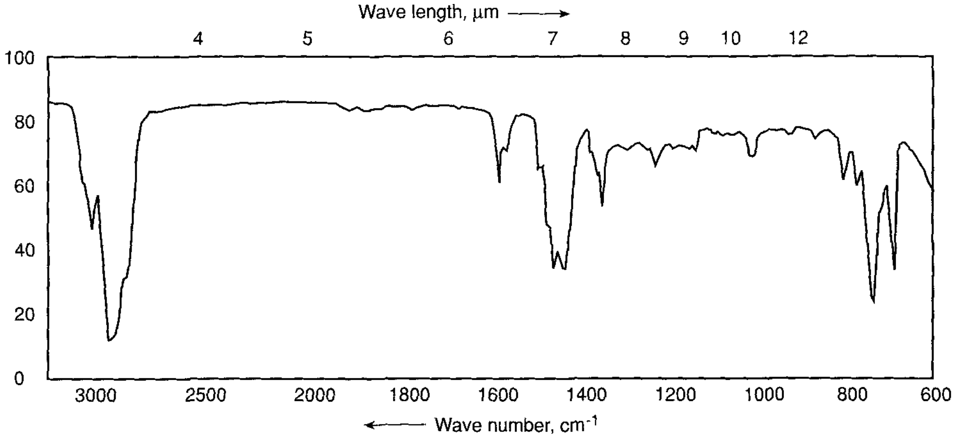


Figure 4.19 Infrared spectrum of an aliphatic/aromatic resin

The characteristic absorption bands of the carboxyl group occur in the region 2500–3000 cm^{-1} (hydroxyl) and ca. 1700 cm^{-1} (carbonyl).

Additionally, IR spectral analysis allows one to identify the resin type, i.e., aromatic, aliphatic or mixed type. An example is given by the spectrum of a mixed aliphatic/aromatic resin. Aromatic structure is characterized by a weak absorption at 3030 cm^{-1}, together with absorptions around 1600 and 1500 cm^{-1} and below 900 cm^{-1}. Other absorptions are less characteristic. The typical absorptions can be identified in the spectrum shown in Figure 4.19.

As each resin has its own "fingerprint" spectrum, IR spectroscopy may be considered as a physical characteristic, on condition that it is recorded under strictly controlled conditions. Typical spectra of resins may be found in a number of IR compilations.

4.2.18.2 Ultraviolet Spectroscopy

UV spectroscopy may be used to distinguish aromatic from aliphatic resins. The UV spectrum of an aromatic resin is shown in Figure 4.20. Characteristic absorptions occur in the region of 265 and 275 nm.

The main use of UV spectra of resins is to provide data used by tire manufacturers as quality standards.

4.2.18.3 Nuclear Magnetic Resonance Spectroscopy

Proton nuclear magnetic resonance – (NMR-H) – is very useful for quick identification of resins. NMR spectra permit one to identify and to quantify aliphatic and aromatic protons. Aliphatic protons give peaks in the region 1–2 ppm, aromatic protons in the region 7 ppm. The proportion of aromatic to aliphatic protons helps in classifying resins.

As an illustration, the spectra of three different resins are respresented in Figure 4.21.

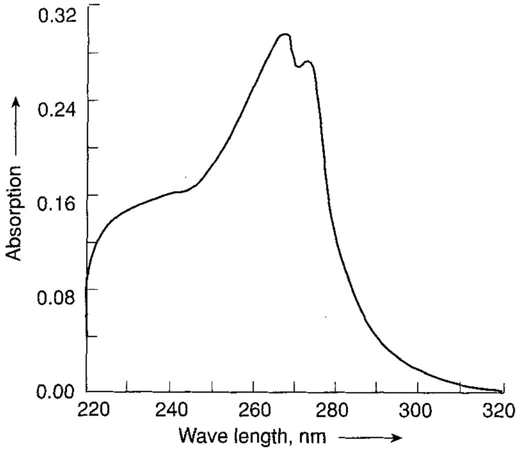


Figure 4.20 Ultraviolet absorption spectrum of an aromatic resin

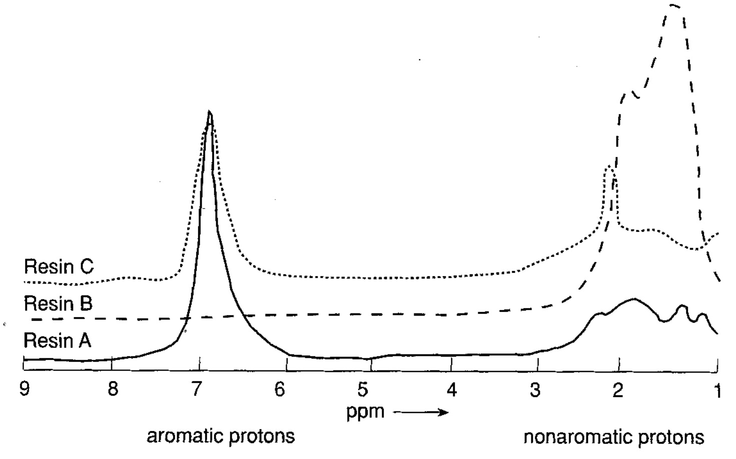


Figure 4.21 Proton magnetic resonance spectrum of three resins

Resin A: aromatic resin from pure monomers (α-methylstyrene/o-vinyltoluene), proton ratio aromatic/aliphatic = 1.25

Resin B: fully hydrogenated aromatic resin, proton ratio aromatic/aliphatic = 0

Resin C: C_5/C_9 resin from cracker fractions, proton ratio aromatic/aliphatic = 0.49

4.3 Summary of Properties of Resins

Tables 4.7-4.13 list typical properties of various types of hydrocarbon resins [4.14].

Table 4.7 Typical properties of aromatic resins

Property	Coal-tar-based	Petroleum-based
Softening point, °C R & B	liquid to 170	liquid to 130
Gardner color	6-18	5-12
Iodine number, $gI_2/100$ g	35-105	25-90
Density, g/cm^3	1.08-1.15	1.06-1.11

Table 4.8 Typical properties of resins from pure aromatic monomers

Property	Styrene	α-Methylstyrene	α-Methylstyrene/vinyl-toluene
Softening point, °C R & B	liquid to 160	70-145	75-120
Gardner color	1-3	< 1	< 1
Bromine number, g $Br_2/100$ g	0	2-8	2
Density, g/cm^3	0.98-1.08	1.06-1.07	1.05

Table 4.9 Typical properties of aliphatic petroleum-based resins

Property	C_5-olefin-diolefin resins	Piperylene resins	Dicyclo-pentadiene resins
Softening point, °C R & B	70-100	liquid to 115	90-120
Gardner color	5-7	3-7	5-7
Bromine number, g $Br_2/100$ g	15	25	60
Density, g/cm^3	0.93-0.97	0.88-0.97	1.1

Table 4.10 Typical properties of terpene resins

Property	Derived from α-Pinene	β-Pinene	D-Limonene
Softening point, °C			
R & B	25–135	10–135	100–135
Gardner color	3–5	1–4	1–4
Bromine number,			
g Br_2/100 g	25–30	15–30	27–28
Density, g/cm^3	0.90–0.98	0.93–0.99	0.99

Table 4.11 Typical properties of mixed resins

Property	C_5/C_9 resins	Terpene-aromatic resins
Softening point, °C R & B	liquid to 105	105–115
Gardner color	2–10	2–5
Iodine number, g I_2/100 g	< 25	not available
Density, g/cm^3	0.86–1.07	1.02

Table 4.12 Typical properties of phenol-modified resins

Property	Based on C_9 and indene-coumarone	Terpene
Softening point, °C R & B	liquid to 120	95–155
Gardner color	5–8	4–11
Hydroxyl number, mg OH/g	56–112	80–260
Density, g/cm^3	1.08–1.1	1.03–1.09

Table 4.13 Typical properties of hydrogenated resins

Properties	Based on DCPD	C_9 Fraction	Aromatic monomer	Terpene
Softening point,				
°C R & B	85–140	70–140	liquid to 125	85–115
Garnder color	< 1	< 1	crystal clear	< 1
Bromine number,				
g Br_2/100 g	2–3	not available	not available	10–20
Density, g/cm^3	1.10	0.98–0.99	0.92–1.04	0.94–1.01

5 Applications

Hydrocarbon resins are used in many areas of application. They are seldom used alone, but mostly in conjunction with other materials to achieve specific properties. These specific properties may be used to classify such resins:

- Hard resins, mainly in the paint and varnish industry
- Plastisizers and compounding agents, in the plastics industry (rubber and PVC compounding)
- Tackifying resins in adhesives
- Fixing agents in wood protection
- Water repellents in various types of applications

In some areas of application, the use of resins has been well established for decades, for instance in rubber compounding or adhesives. Other areas may not be so well known; they have developed with improvements and diversification of hydrocarbon resins.

The most important uses are in adhesives, e.g. in construction, hot-melt and pressure-sensitive adhesives (PSA), followed by coatings, tires and mechanical goods, printing inks, and to a less extent in various other industrial fields.

In several applications, modified and unmodified hydrocarbon resins are still in competition with the traditional rosin and rosin derivatives. These areas are mainly adhesives, printing inks, and coatings. The most important rosin consumption is, however, in paper sizing and emulsifier production; these applications are not treated here.

The main application areas, by resin type, are:

- Aliphatic C_5 hydrocarbon resins (all types) in rubber compounding, adhesives, traffic paints, and coatings
- Aromatic resins (C_9, indene-coumarone) and mixed C_5/C_9 hydrocarbon resins, largely used in rubber and adhesives, a little less in coatings
- Terpene resins, almost exclusively used in high-grade adhesives
- Dicyclopentadiene resins, used in some coatings, and modified types in the printing ink, and rubber industry

Even now, evaluation of the suitability of resins for use in various fields of application is mainly based on more or less empirical data. However, efforts are under way to associate application properties with more basic characteristics of particular resins. Most of this work is done by resin producers. More basic research work in this direction by universities and research institutes would be of great value.

It should be stressed at this point that the following survey, though covering the most important applications, can by no means be complete.

The principal aim of this chapter is to provide a general understanding of why indene-coumarone and petroleum-based hydrocarbon resins are of interest in widely differing

industrial applications. Whenever possible, some explanation is given as to how the resins are used, which characteristics can be influenced, and the effect the resins may exert on the various systems in which they are to be incorporated.

It goes without saying that all technical information, data and instructions concerning function and application of the resins are to be considered empirical data, and that no warrenty is given. Resin users must carry out their own evaluations to determine the suitability of particular resins for their specific applications.

5.1 Adhesives

Adhesives (glues) have been known for thousands of years. As early as 4500 BC the Sumarians used some sort of asphalt as an adhesive binder material. By 3500 BC, the Sumerians were using glues made from animal skin. Around 300 BC the use of colophonium resins from birch bark was discovered. Similar systems, together with glues based on cheese, fish, and bone were used by ancient Egyptians, Greeks, Romans, and Normans. The first "modern" adhesive, based on natural rubber was used in 1823, a year which marks the beginning of the adhesive industry in today's sense of the word.

The adhesive systems available today can be differentiated into two main groups. Natural adhesives include various types of animal glues, the dextrins, and caseine-based adhesives.

Synthetic adhesives, may be subdivided into the following three groups:

- Adhesives based on thermosetting raw material, such as urea- and phenol-formaldehyde, epoxy, or anaerobic adhesives
- Adhesives based on thermoplastic raw material, such as polyvinyl acetate, acrylics, cyanoacrylics, polyolefins, polyamide, styrene-butadiene or styrene-isoprene block copolymers (thermoplastic rubber)
- Adhesives based on elastomeric raw material, such as styrene-butadiene rubber (SBR), polychloroprene, nitril rubber, polyurethane

Most synthetic adhesives are formulated from a "backbone" polymer, a tackifying resin, and a "carrier" to give the necessary consistency for a given application, which may be solvent, water, or heat. Synthetic adhesives may be classified according to the "carrier" as:

- Solvent-borne or contact adhesives, typical examples being natural rubber, SBR, or neoprene-based types
- Dispersed or water-based adhesives, for which the polyvinylacetate dispersions are characteristic
- Hot-melts, for which typical examples are the ethylene/vinylacetate (EVA) copolymer-based systems

The following commonly used classification is not very systematic, as it refers more to the application area or special properties of the adhesive:

- Solvent and water-borne adhesives
- Hot-melts
- Pressure sensitive adhesives (PSA)

Of course, there are other adhesive systems, but the following discussion concentrates only on these, as they account for the major use of resins in adhesives, and are thus the most relevant for the adhesive types discussed later in this chapter.

Resins (tackifiers) are added to the backbone polymers to improve the stickiness (tack), specific adhesion, and wetting, in short to regulate rheological properties of the final adhesive system.

The most commonly accepted definition of tack is the ability of two similar materials to resist separation after their surfaces have been brought into contact for a short time under light pressure [5.1]. The oldest and simplest test is simply to feel the adhesion of a material, applied and pressed together between fingers and thumb. More reliable tests have been developed:

- Quick Stick 90° (PSTC-11) [5.2]
  The test measures the force resisting peeling of a tape at a 90° angle from a standard surface on which the tape is applied under its own weight.
- Peel Adhesion for Single-Coated Tapes 180° (PSTC-1/AFERA 4001-PB) [5.3]
  The test measures the force needed to remove a tape from a panel or its own backing at a specific angle and speed.
- Shear Adhesion Failure Temperature (SAFT) (PSTC-1/AFERA 4012-P1 modified)
  The test measures the temperature at which a standard area of tape is pulled off a test panel under a constant load and increasing temperature.
- Rolling Ball Tack (PSTC-6)
  The test measures the distance required to stop a steel ball from rolling under specific conditions.
- Polyken Probe Tack (ASTM D 2979)
  This test measures the force needed to break adhesive bond with a machine that pushes the tip of a flat probe onto the adhesive at controlled rates, pressures, and dwell times.

Tack depends on the type of resin, molecular mass (softening point or glass transition), and resin concentration. Normally, low molecular mass resins bring maximum relative tack

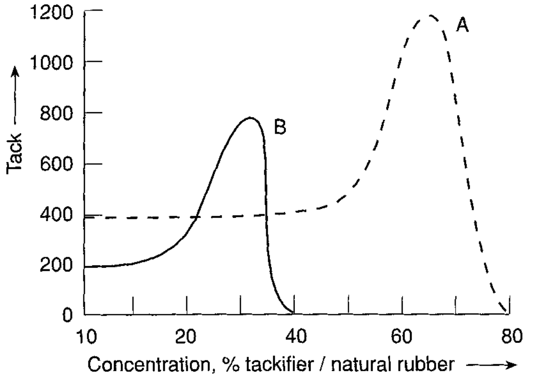


Figure 5.1 Effect of tackifier concentration and molecular mass tack.
A: Low molecular mass resin; B: High molecular mass resin

at higher concentrations, whereas higher molecular mass resins give maximum relative tack at lower concentrations but at a lower absolute tack level, as shown in Figure 5.1.

Cohesion increases with resin molecular mass and concentration. Some details of the influence of resin characteristics and concentration on tack, via determination of viscoelastic properties, are given in Section 5.1.3.

5.1.1 Solvent- and Water-Borne Adhesives

The carrier for these adhesives may be an organic solvent or water, i.e., the backbone polymer is carried either in solution or in dispersion. In general, solvent-borne adhesives are easier to formulate. They spray and wet better, dry faster, or offer a wider range of drying and open time than do water-borne adhesives.

These days however, the trend is toward water-borne systems, mainly because of occupational health risks (toxicity and inflammability of solvents) and cost. In some applications, mainly in construction (e.g. carpet installation) solvent use is more or less prohibited. In other applications, e.g., in shoe-making, only solvent-borne adhesives comply with the high requirements of the industry. Therefore, solvent-based adhesives are always used and appropriate equipment is installed to exhaust and recycle the solvent.

5.1.1.1 Solvent-Borne Adhesives (excluding pressure-sensitive adhesives)

The choice of an appropriate solvent depends on the polymer type, cost, and properties of the solvent (toxicity, solubility, ease of removal). The more frequently used solvents are chlorinated solvents, hydrocarbons, esters, and ketones. The main backbone polymers combined with tackifying resins are SBR or polychloroprene rubber.

Tackifiers for these adhesives are hydrocarbon resins (aromatic, including indene-coumarone resins; aliphatic, and mixed C_5/C_9 resins), rosin and rosin esters, terpene-phenolic resins, and *tert.*-butylphenol resins. The latter are claimed to improve the temperature resistance of the adhesive coating to some extent.

SBR-based adhesives make use of hydrocarbon- and rosin-based resins; polychloroprene-based adhesives use essentially phenolic resins blended with aromatic hydrocarbon resins.

Elastomers, having relatively high molecular mass and thus high viscosity, often require tackification, depending mainly on the base polymer type and also on the projected end use. Selection of tackifying resin is subject to the following criteria:

- Compatibility with the backbone polymer
- Properties such as softening point, color, thermal stability, odor
- Influence of other compounds in the formulation
- End use requirements, such as initial tack, open time, cohesion

Styrene-butadiene rubber (SBR) is the most widely used elastomer. A typical formulation is given below:

- SBR	10–15 wt%
- Tackifier	1–20 wt%

- Plasticizer 1- 5 wt%
- Fillers 25-35 wt%
- Solvent 30-40 wt%

Tackifying resins enhance tack and may reinforce cohesion. Resin types used are, in decreasing order, aromatic resins, rosin and rosin esters, C_5/C_9, and some C_5 resins.

Other styrene elastomers used as backbone polymers in solvent-borne adhesives are block copolymers such as styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), and styrene-ethylene-butene-styrene (SEBS). They are more popular in hot-melt formulations. More details are given in Section 5.1.2.

A typical formulation is as follows:

- SEBS 20-25 wt%
- Tackifier 20-45 wt%
- Adhesion promotor 0.5 wt%
- Stabilizer 0.7 wt%
- Solvent 25 wt%

The tackifiers used are roughly the same as with SBR.

Another important group of solvent-borne adhesives is polychloroprene based. They are usable as adhesives only in combination with tackifying resins. Normally, these are alkylphenolic or terpene-phenolic resins, often blended with polyisocyanates to ensure good cross-linking with the reactive groups of polychloroprene. Addition of these resins improves the adhesive properties.

By further adding thermoplastic resins, such as aromatic C_9 hydrocarbon resins, indene-coumarone resins, or terpene resins, the so-called open time is extended, i.e. the period during which the solvent has entirely evaporated, but the final bonding has not yet been fully achieved. Cohesion is improved and adhesion enhanced. Addition of thermoplastic resins also lowers the solution viscosity. This allows relatively high resin loading, thus reducing cost while maintaining high quality.

There is no single optimum formulation or additive resin. In practice, the following resin combinations have given good results:

- Indene-coumarone or C_9 resins with a high indene content, having a softening point of 145/150 °C R & B, to produce a formulation with a relatively high upper service temperature
- Indene-coumarone or corresponding resins with a high indene content, softening point 100/120°C R & B, in combination with a hard resin, softening point 145/150 °C R & B; good tackiness is enhanced by the 100–120 °C R & B resin, and good upper service temperature is obtained by the 145/150 °C R & B resin; a single intermediate type does not give the same positive effect.
- Phenol-modified indene–coumarone resins, which do not improve the upper service temperature, but because of their properties (which in some ways resemble those of wood rosin), they increase the tackiness and speed up the adhesive strenght by means of their more polar nature. They are particularly suitable when using solvent blends based on alcohol, esters, etc., in flooring adhesives.

There is no point in giving detailed formulation instructions, since the formulation depends largely on the type of application. Furthermore, combinations between the base

elastomers (e.g., neoprene), alkylphenol resins, indene-coumarone or hydrocarbon resins, etc., can be formed in various ways. Nevertheless, tentative formulations for guidance are given in Table 5.1. It is recommended that further instructions are taken from data supplied by synthetic rubber manufacturers.

Table 5.1 Suggested formulations of solvent-borne adhesives (parts per weight)

Example A		Example B	
Position 1 (for mastication)		Polychloroprene, masticated	100
		Magnesium oxide, extra light	4
Polychloroprene	2.5	Zinc oxide, activated	4
Magnesium oxide	0.8	Silica	20
Zinc oxide, activated	0.2	IC resin, 145/150 °C R & B	50
		Chlorinated rubber	10
Position 2		Antioxidant	2
Polychloroprene type 1	2.3	Toluene	90
Polychloroprene, type 2	10.0	Benzene 65/95 °C	180
Alkylphenol resin	5.5	Ethyl acetate	180
Basic reactive alkylphenol resin	1.0		
Indene-coumarone resin 145/150 °C R & B	2.0	Ratio of solvent used: 1:2:2 The viscosity of the resulting adhesive is adjusted to 45 P	
Position 3			
Water	0.2		
Toluene	20.0		
Ethyl acetate	14.0		
Methyl-ethyl-ketone	10.0		
Benzene 60/95	30.8		
The adhesive is processed without crosslinking agents.			
Open time:	ca. 30 min		
Bending time: 140 °C on sole rubber			
Viscosity: outflow according to DIN 53 211, 60 s, DIN beaker 8.90 cm^3			

A suggested formulation for a floor covering adhesive (parts per weight) is:

- Polychloroprene type 1	40
- Polychloroprene type 2	60
- Silica	10
- Magnesium oxide, extra light	4
- Zinc oxide, activated	4

The polychloroprene is passed repeatedly through water-cooled, narrowly adjusted mixing rollers until a closed sheet is formed. First the silica, then the magnesia, and finally the activated zink oxide is worked into the sheet on the rollers. The time allowed for mastication and for adding the metal oxides depends on the type and size of the roller mill and the quantity of polychloroprene to be processed in one batch. When using mixing rollers with a roller length of 1500 mm, a diameter of 665 mm, a friction of 1:1:1, and a rotational speed of 24 m/min, 25 kg of polychloroprene can be treated to form the finished sheet within 20 min. The finished sheet, together with the resin, is then brought into solution. A typical composition (parts per weight) is:

- Polychloroprene sheet	24.0
- Alkylphenol resin	2.4
- C_9 hydrocarbon resin (145/150 °C R & B)	7.2
- Antioxidant	0.4
- Solvent mix	66.0

A suitable solvent mix is blended of ethyl acetate, gasoline 65–95 °C, and toluene in a ratio of 2:2:1. The viscosity of the adhesive should be ca. 200 mPa · s.

5.1.1.2 Water-Borne Adhesives

For environmental protection reasons, there is a distinct trend away from solvent-based systems. Many adhesive problems formerly solved by solvent-based adhesives can now be solved with hot-melts or water-based systems, but not all of them. It is obvious that the use of hot-melts requires specific equipment, which may not be available in all places where solvent-based adhesives are used. Water-based adhesives, although safe as far as handling is concerned (no vapors from evaporating solvents), do have a number of properties that make their application not quite as simple as that of solvent-based adhesives.

Polymer dispersions, such as polyvinyl acetate (homo- and copolymers), latices (natural and synthetic rubber), or acrylates, find increasing use in the formulation of flooring adhesives, systems for packaging, laminating, various sectors of the automotive industry, and in many other areas. The dispersions as supplied by the raw material manufacturer are seldom used directly as adhesives. Therefore, the diverse requirements of dispersion adhesives, as a rule, necessitate modification of the adhesive system, which is carried out by the adhesive manufacturer.

For modification of basic dispersions based on polyvinyl acetate, acrylates or latices, petroleum hydrocarbon and indene-coumarone resins are widely used, as well as rosin esters, terpene-phenolic resins, polyterpene and ketone resins.

Various methods can be used to incorporate the corresponding resin dispersion in the basic dispersion, depending on whether the preparation of the dispersion has to be solvent-free, or whether an intermediate use of a limited solvent quantity for the preparation of the

resin dispersion is permissible (hybrid adhesive). After preparing the resin dispersion (secondary dispersion), it is added to the basic dispersion (PVA, latex, etc.). Liquid resin types or easily liquified semi-liquid resins (softening point 25 °C R & B) can be incorporated in the basic dispersion directly or after briefly warming. Harder resin types necessitate a preliminary dispersion step.

Apart from the possibility of directly adding a highly concentrated resin solution to the basic dispersion, the incorporation of hard resins requires a predispersion, as already mentioned. Various means are available:

- Preparation of a highly concentrated solution of the resin in toluene, white spirit, etc., and dispersion of the resin solution
- Preparation of the resin solution in a processing oil (for instance spindle oil), and subsequent dispersion
- Preparation of the resin solution in a suitable plasticizer (e.g., dibutyl phthalate), and subsequent dispersion
- Solution of a resin in a liquid resin and subsequent dispersion
- Pressure/heat dispersion of the resin without addition of a solvent

By adding a resin-based secondary dispersion, many system properties can be changed, depending on the specific formulation, for instance, quick wet set, initial grip, physical and chemical resistance, water resistance, adhesion to difficult substrates, contact adhesion, adhesive strength, blocking resistance, hot-seal properties. There are sometimes contradictory requirements. This is why in many cases secondary dispersions are formulated on the basis of resin combinations, in order to obtain optimum results.

The improvements sought by adding hydrocarbon or indene-coumarone resins (principally resistant to water and chemicals) are mainly due to the neutral and strongly hydrophobic character of the unsaponifiable IC and petroleum-based resins. This is the reason for the difficulty of incorporating IC and petroleum-based resins in a water-borne dispersion.

Apart from liquid resins, the solid resins are of importance insofar as, in dispersion adhesive systems, they influence the same properties as they do in solvent-based adhesives. An example is the increase in the upper service temperature (heat stability) by making use of hard resins (for instance, 140/150 °C R & B softening point resins). Apart from that, insufficient adhesive strength is sometimes observed when using only a liquid resin, as the liquid resin does not provide sufficient backbone owing to its too low molecular mass. Therefore, the problem can be solved by a combination of a liquid resin with a hard resin.

A general guide for the quantities of the secondary dispersion could be:

- 40–50 % for natural rubber latex
- 50–60 % for chloroprene latex (or similar)
- 20–25 % for acrylic ester dispersions
- 5–50 % for polyvinyl acetate dispersions

The optimum amount of addition has to be determined individually.

The precondition for the use of petroleum-based and IC resins in secondary dispersions is their compatibility with polyvinyl acetate, acrylates, various other polymer-based substances, and latices. A wide variety of hydrocarbon resins show good compatibility; no phase separation occurs. After water evaporation, the films are transparent. Only in very rare cases a slight opalescence may be observed, but there is no indication of phase separation.

When using resin-containing dispersion adhesives for bonding of PVC films and similar materials, it is very important that no lower molecular mass components of the resin from the dispersion adhesive, modified with a hard resin, migrate through the substrates to be bonded or it will lead to staining. Tests, run even at elevated temperatures, should show no migration effect.

Addition of a resin solution, for instance, in toluene, to the polyethylene-polyvinyl acetate dispersion may lead to a slight thickening. The original viscosity is easily restored by addition of water.

The molecular mass distribution of the elastomer component of a basic dispersion (which should be relatively wide) also plays an important part. As a rule, the added resin component dissolves the lower molecular mass portion of the elastomers and creates tackiness, while the undissolved higher molecular mass part of the elastomer maintains the cohesive strength. Furthermore, resin and polymer should have similar solubility characteristics if a resin acts as a tackifier.

It is further important that the glass transition temperature, T_g, of the resin/elastomer blend is within a specific temperature range; this is of particular importance for pressure-sensitive adhesives. This can be achieved, for instance by blending a hard resin of high glass transition temperature with an elastomer with low T_g.

Naturally, the selection of an opimum resin or optimum resin combination depends on the effect sought by adding the secondary dispersion. Principally thermoplastic, nonreactive, unsaponifiable resins with a relatively low molecular mass, such as petroleum-based and indene-coumarone resins are used. They are generally characterized by their hardness and resistance to chemical and physical influences. The result is mainly determined by the quantity added and the softening point, the quantity being dependent on the degree of hardness. As an example, resins with a higher melting point will show high peel and shear resistance while the tackifying properties are somewhat lower. Lower melting resins will show the reverse properties. They are to be considered universal tackifying resins. Block resistance increases in the sequence rosin esters, terpene-phenolic resins, polyterpene resins, hydrocarbon resins, indene-coumarone resins, while adhesion decreases. A higher resin content increases the adhesion, film elasticity, and sealing properties. However, it does restrict the resin quantity that can be added to the formulation.

On the basis of their properties, a great number of resins can be considered for use as a resin component. However, without exact knowledge of the characteristics of the basic dispersion and of the properties to be obtained by the modification, the suggestion of an optimum resin type is hardly possible. Nevertheless, it is possible to give some indications as to the resin types to be selected, based on experience. For example:

- Indene-coumarone resins:
  softening points 80, 100, 150 °C R & B. The two high-melting resins have a positive effect on the upper service temperature of the system
- C_9 petroleum-based resins, indene-containing, balanced composition; softening points 80 and 100 °C R & B; widely used resin types, separately or in combination
- C_9 petroleum-based resins, higher percentage of α-methylstyrene/vinyltoluene; softening points 100 and 120 °C R & B. Nonstaining resins for thin PVC floor and wall tiles

- C_4-modified indene-coumarone resins; softening points 100 and 120 °C R & B. Used separately or in combination
- Indene-coumarone resins; liquid or low softening point (30 °C R & B) for direct blending
- Liquid resins; without addition of a hard resin, sometimes unsatisfactory because of insufficient tack

Summarizing, it can be stated that indene-coumarone and aromatic petroleum-based hydrocarbon resins are suitable as blending resins in the formulation of dispersion adhesives.

Special attention has to be drawn to the so-called staining effect when using hydrocarbon resins in flooring adhesives, for instance, for PVC floor tiles. Careful selection of resin is necessary to avoid staining or discoloration. This can be observed on the tile surface, especially in the case of comparatively thin floor tiles, wall coverings, etc., used as substitute for ceramic material. This staining effect, noticeable after a period of exposure to light, can be due to the presence of a higher oligomer content in the resin which can migrate to the surface.

These considerations determin the type of resin to be used in adhesives for thin PVC flooring material:

- A resin with a narrow molecular mass distribution and a low oligomer content
- A resin based on unsaturated compounds with low sensitivity to visible/UV light

Two resin types show good performance in this line of application:

- C_9 hydrocarbon resin, isothermally polymerized, high content of α-methylstyrene/vinyltoluene; softening point 100 °C R & B
- as above, but aliphatic-modified; softening point 100 °C R & B

Similar results can be obtaine using modified C_5 hydrocarbon resins.

There are a number of preliminary tests to determine the extent to which construction and flooring ahdesives accellerate surface staining of vinyl flooring. The principles of a testing method is briefly outlined:

A 10 × 10 cm^2, light colored (preferably white) flooring sample is placed face down on a clean surface. A thick, even coat (5 cm strip) of the adhesive to be tested is applied to the back of the tile with a calibrated coating device (e.g., a draw-down bar) and allowed to dry for 24 h. The samples are then conditioned in an oven at 65 °C for 24 h, with the exception of retained samples. The conditioning serves to expedite possible migration of light-sensitive resin components to the surface of the tile. The samples are then exposed to UV light for 24, 36, or 48 h, followed by a further 2 h conditioning period at ambient temperature before taking readings. The test samples and the unconditioned control samples are then examined visually against each other for the degree of staining or discoloration.

5.1.2 Hot-Melt Adhesives

In this case, neither solvent nor water is needed to activate the adhesive. The solid adhesive is liquified by heating, and is applied to one or both faces of the substrate, where the adhesive bond is formed as soon as the melt cools down and solidifies.

There are many advantages of such systems in comparison with solution systems:

- smaller volumes, no solvent or water has to be transported and handled
- no evaporation of solvent, environmental effect and recycling are avoided
- no time required for evaporation, quick sticking

On the other hand, the systems are reversible by application of heat, and can not be applied to heat-sensitive substrates.

Industrial hot-melts are applied by appropriate equipment; in the do-it-yourself sector or in some special applications with a heated "gun".

The base polymers, used in conjunction with tackifying resins for the formulation of hot-melts are:

- Ethylene/vinyl acetate copolymer (EVA)
- Styrene block copolymers, such as styrene-butadiene-styrene (SBS), and styrene-isoprene-styrene (SIS)
- Polyethylene
- Polypropylene

Polyester and polyamides are also employed in hot-melts, but do not need tackifying resins, and are therefore not considered here.

The high molecular mass backbone polymers, even in the molten state, are deficient in tack, so they are not suitable for use as adhesives, which must have excellent tack, they must flow readily when molten, and possess good stability at working temperatures. They must set and develop high strength very rapidly (very short open time). Finally, they must have good mechanical properties, and, last but not least, they should also be cheap.

A typical hot-melt system contains the following major components:

- the backbone polymer or copolymer, such as ethylene/vinyl acetate block copolymers, or polyolefins
- a paraffin/wax, for instance, microcrystalline waxes or similar, as a viscosity-lowering agent
- tackifying resins, hydrocarbon resins, rosin esters, terpene-phenolic resins, which also act as viscosity-lowering agents
- fillers/pigments

On the basis of empirical knowledge, the following observations have been made:

- high concentration of base polymer leads to a high melt index and viscosity, improves mechanical properties (tensile strength and hardness) and reduces open time
- high tackifying resin concentration lowers the melt index and viscosity, but has an adverse effect on mechanical properties. Tack is improved and open time increased

- high wax concentration lowers melt index and viscosity, but adversely affects tack and mechanical properties; by diffusion to the surface, wax molecules prevent blocking between two coated surfaces.

Considering all these effects, numerous possibilities for the formulation of hot-melts are available to the industry. Optimization has to be carefully worked out with regard to application requirements.

Within a given type of backbone polymer different grades are available. Generally, increase of molecular mass decreases compatibility, but increases melt index, viscosity, and mechanical properties.

Tackifying resins of various types for hot-melt formulations are available commercially. These are mainly:

- Hydrocarbon resins
  - aliphatic C_5
  - aromatic C_9, and from pure monomers
  - aliphatic/aromatic C_4/C_9 and C_5/C_9
  - hydrogenated types
  - polyterpene and hydrogenated types
- Rosin and rosin esters
- Terpene-phenolic resins

Hydrocarbon resins are by far the most used tackifiers, (ca. 70 %). Rosin and rosin esters account for about 20 %, the rest being terpene-phenolic resins.

To meet specific requirements, blends of different resin types are often used. Choice depends on the backbone polymer and desired application performance.

Hot-melts are used as adhesives (HMA) and as coatings (HMC). They are also used as pressure-sensitive adhesives (HMPSA) which are described in Section 5.1.3.

The most frequently used backbone polymer is ethylene/vinyl acetate (EVA). Block copolymers, introduced more recently, are being used to an increasing extent. Application of polyolefins is not so widespread.

5.1.2.1 EVA-Based Hot-Melts

EVA polymers are available with a wide range of vinyl acetate content (18–40 %), molecular mass and thus melt index.

Compatibility with hydrocarbon resins increases with increasing vinyl acetate content, and decreases with molecular mass and EVA concentration. An example is given in Table 5.2, using a C_5/C_9 resin, softening point 95 °C R & B.

In some applications, especially in woodworking adhesives (see Section 5.1.2.1.2) a borderline compatibility (controlled incompatibility) may be preferred, provided there is no phase separation. C_9 resins with a relatively high indene content and softening points between 100 and 155/160 °C R & B are used.

Table 5.2 EVA/hydrocarbon resin compatibility

Vinylacetate content, %	Melt index g/min	EVA/hydrocarbon resin 75/25	50/50	25/75
40	48– 66	A	A	A
33	38– 48	A	A	A
28	365–440	A	A	A
28	134–168	A	A	B
28	38– 48	A	A	B
28	22– 28	A	A	C
28	5.3–6.7	A	A	C
28	2.6–3.4	A	C	C
25	365–440	A	C	C
25	17.3–20.9	A	C	C
25	1.7–2.3	A	D	D
18	455–550	D	D	D
18	136–165	D	E	E
18	2.2–2.8	E	E	E

Compatibility temperature, °C:
A = < 25 B = 25–100 C = 100–150 D = 150–200 E = > 200

Hot-melt adhesives based on EVA are mainly used in the following areas, mostly on fully automated production lines:

- Packaging
- Woodworking
- Bookbinding
- Nonwoven fabrics and clothing

Packaging uses by far the largest quantities of hot-melts.

5.1.2.1.1 Packaging

Application areas include sealing of cases and cartons (most important), tray forming, but also bottle and can labeling. The advantage of hot-melts is instantaneous bonding, allowing high production rates.

A general basic formulation is:

- EVA (28 % VA, MI 365-400) 40%
- Hydrocarbon resin (C_5/C_9 type, 95 °C R & B) 50%
- Microcrystalline wax 10%

5.1.2.1.2 Woodworking

The main use for hot-melt adhesives in woodworking is in edge veneer and, more generally, to fix wood veneer to chipboard, fiberboard, or similar materials in the furniture

industry. Another use is a "temporary adhesive" in the industrial production of decorated furniture, where the decorative panel is fixed by sticking (e.g., cupboard doors). During the relatively long drying time of the usually water-borne basic adhesive, the pieces must be held together to allow further handling. To achieve this a hot-melt is applied for quick fixing to allow immediate handling and higher machine speeds.

The main resin types used are C_9 resins with a high indene content, with softening points of 120, 140, 145/150, and 155/160 °C R & B. In smaller quantities, and added in most cases merely for the correction of the viscosity, are the resin types with softening points 100 and 110 °C R & B.

For the formulation of edge-bonding hot-melts, good heat resistance is required, which as a rule necessitates as high a softening point as possible. On the other hand, too high a melt viscosity is undesirable, as this makes processing and application considerably more difficult.

The melt viscosity of the resin to be manufactured first depends on the resin-forming components. Depending on the origin of the starting material, and the preselection of the fractions extracted for resin formation and their combinations, those individual components of the resin which are less compatible with hot-melt components produce a higher viscosity, whereas resin components more compatible with hot-melt components produce a lower viscosity. On the other hand, for good adhesive qualities, a resin with maximum compatibility is not so desirable as a resin with partial compatibility, as mentioned earlier. Therefore, finding the best compromise is a major task.

Many resin manufacturers offer suitable resins, as they have been able – within fixed limits – to achieve viscosity regulation via the production method itself, by preserving the partial compatibility required for hot-melt applications. An example is the high-indene C_9 resin, softening at ca. 150/155 °C R & B.

Experience has shown that, in this softening point range, a shift in the softening point of even 2–3 °C can influence the melt viscosity to a great extent. Therefore, in view of the normal deviation (tolerance) of ± 5 °C, manufacturers select a very high melting resin in a narrower melt range to obtain the best flow characteristics, combined with the highest heat resistance.

Woodworking hot-melts are formulated with one or more EVA types, tackifying resins and fillers, which are included to improve cohesion, to control color, and to reduce cost. A representative formulation is:

– EVA (33 % VA, MI 38–48)	15%
– EVA (28 % VA, MI 365–440)	15%
– Hydrocarbon resin (C_5/C_9 type, 95 °C R & B)	20%
– Filler (e.g. chalk)	50%

5.1.2.1.3 Bookbinding

Bookbinding hot-melts formulated on the basis of EVA contain less wax than packaging hot-melts. Such formulations have higher viscosities, and thus require higher application temperatures. Tackifiers for such uses must have good heat resistance. Aging resistance is also important. The aging process, effective by oxidative attack on the resin, causes the

resin component to become brittle over the service life. In bookbinding, this means that the spine of a book may become detached, owing to the increasing brittleness of the adhesive bond, often observed in old books.

For these reasons, higher-priced, high-quality resins are used, e.g., terpene-phenol resins or hydrogenated hydrocarbon resins, but also to a lesser extent the less-expensive rosin esters, C_5, C_4/C_9, C_5/C_9, and C_9 resins, depending on the intended use. High-quality hot-melts are required in more valuable cloth-bound hardback books, while a somewhat lower quality standard is perfectly sufficient in the binding of paperback books, directories, catalogs, and similar items of lower expected lifetime.

For higher-quality bonding, where the classical polyvinyl acetate adhesives are used, hot-melts may be applied for temporary assembly, allowing higher machine speeds.

5.1.2.1.4 Nonwoven Fabrics/Clothing

Disposable applications comprise diapers and napkins in baby care and sanitary pads; the main area is disposable diapers assembly. Adhesives are mainly based on EVA, but block copolymers are increasingly used.

Because of the negative consumer reaction to yellow-colored resins, diaper assembly uses, almost exclusively, noncolored resins, the so-called water-white resins, produced from pure monomers or hydrogenated hydrocarbon resins. More recently, less expensive styrene-terpene resins have been produced in the United States.

5.1.2.1.5 Other Applications

EVA hot-melts are also used in many other applications. Examples are carpet backing, carpet seaming tape, and temporary assembly, for instance in the shoe and furniture industry, and in the assembly of musical instruments.

5.1.2.2 Block Copolymer-Based Hot-Melt Adhesives

In contrast to the usual polymers, where comonomers are distributed statistically, styrene block copolymers are composed of segments of homopolymers: a hard, thermoplastic, styrene part and a rubbery, elastic, aliphatic part. Such polymers have two glass transition temperatures. In the solid state, styrene blocks associate to form domains, also called "endblock" (Fig. 5.2) comparable to vulcanized rubber, but reversible by heat.

So these polymers are often referred to as thermoplastic rubber (TR). The aliphatic part (i.e. the more elastic network) forms the "midblock".

The most usual types for the adhesive industry are:

- Styrene-butadiene-styrene block copolymer (SBS)
- Styrene-isoprene-styrene block copolymer (SIS)
- Styrene-ethylene-butene-styrene block copolymer (SEBS)

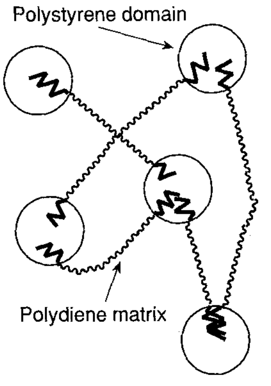


Figure 5.2 Phase structure in SBS and SIS block copolymers

SBS is mainly applied in hot-melt adhesive (HMA) systems, SIS more in hot-melt pressure sensitive adhesive (HM-PSA) systems. The range of TR block copolymers comprises types of higher and lower styrene content, up to 40 %, and variable molecular mass.

These block copolymers, having no "natural" tack, are compounded with tackifying resins. Plasticizing mineral oils, sometimes already incorporated by the TR producer, may be used to reduce melt viscosity and to enhance adhesion.

Choice of tackifying resins is guided by the following observations:

- Aliphatic and alicyclic resins such as C_5, terpene and hydrogenated resins, as well as the rosin derivatives, associate with the rubbery, elastomeric, aliphatic part of TR (midblock), thus enhancing tack
- Aromatic resins, such as C_9, indene-coumarone, and resins produced from pure aromatic monomers, associate with the aromatic styrene domains (endblock), thus reinforcing mechanical properties, such as tensile strength and elastic modulus.

Resins associated with the endblock can increase or decrease the upper glass transition temperature (T_G), depending on the softening point of the resin, thus increasing or decreasing the upper service temperature of the copolymer/resin blend. The effect of reinforcing resins on tensile strenght of a standard SBS block copolymer is demonstrated below [5.4]:

Creep resistance and heat stabiltity may also be improved. The softening point of the reinforcing resin should be higher than that of the styrene domains. Aromatic resins with

Ingredient	Polystyrene domain T_G, °C	Ultimate tensile strenght at 23 °C	at 80 °C
SBS block polymer	ca. 95	33	0.8
SBS + 75 phr IC resin	ca. 120	36	1.6

low softening points are of no use. To balance tack and strength properties, mixtures of aliphatic and aromatic resins are mainly used. Mixed resin types, such as C_5/C_9 hybrids, combine more or less both effects.

Depending on relative concentration, most resins are compatible with styrene block copolymers. In order to determine with which of the two phases - polydiene midblock or polystyrene endblock - the resin is compatible, an easy preliminary test is available. Blends (1:1) of toluene solutions (50/50) of the respective resin with (a) a polystyrene homopolymer and (b) a polybutadiene homopolymer are poured on a glass slide. After evaporation of the solvent, the remaining film is evaluated visually. A clear film indicates compatibility of the resin with the respective phase, a cloudy film indicates incompatibility.

The endblock associating resin (B) leads to a high kinetical stress modulus, an observation of interest in adhesive formulations [5.5]. Addition of an aromatic resin will develop and control initial yield. Forementioned criteria is an indication that addition of an aromatic resin enhances the volume fraction of the styrene domains. On the other hand, modified wood rosin (C) and aliphatic hydrocarbon resins preferentially associating with the elastomeric midblock phase, will increase the volume fraction of the midblock and decrease that of the endblock. This is of interest in formulating pressure sensitive adhesives, as they provide aggressive tack (see Fig. 5.3).

Additional examples of the influence of resins on different properties are given in Figures 5.4-5.6 [5.6].

A somewhat tricky aspect of hot-melt systems based on thermoplastic rubber is the sensitivity of the rubber segments to oxidation, especially at the high melt temperatures involved in production and application of those adhesives. This problem is overcome by addition of stabilizers/antioxidants, (see also Section 5.1.2.5). The stabilizer should be added at the earliest possible moment. With saturated ethylene-butene copolymers as the rubber segment, oxidation sensitivity is markedly reduced.

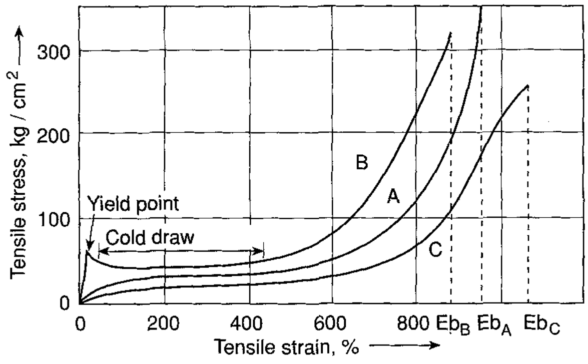


Figure 5.3 Effect of resin type on strain-stress properties

A) SBS thermoplastic block copolymer; B) plus IC resin 50 parts per 100 parts copolymer; C) plus modified wood rosin, 50 parts per 100 parts copolymer

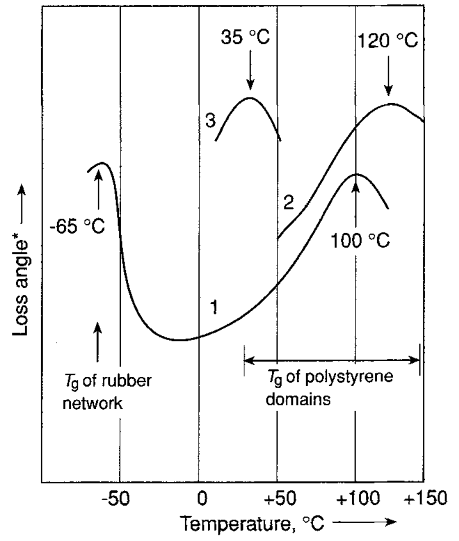


Figure 5.4 Effect of softening point of an aromatic resin on glass transition temperature (T_g)
1) SBS thermoplastic block copolymer; 2) plus IC resin, softening point 145 °C R & B, 75 phr copolymer; 3) plus methylindene resin, softening point 25 °C R & B, 75 phr
** measured on Wallace Dynamic Strain Tester; 8.5 cycles/s; 1 % deformation*

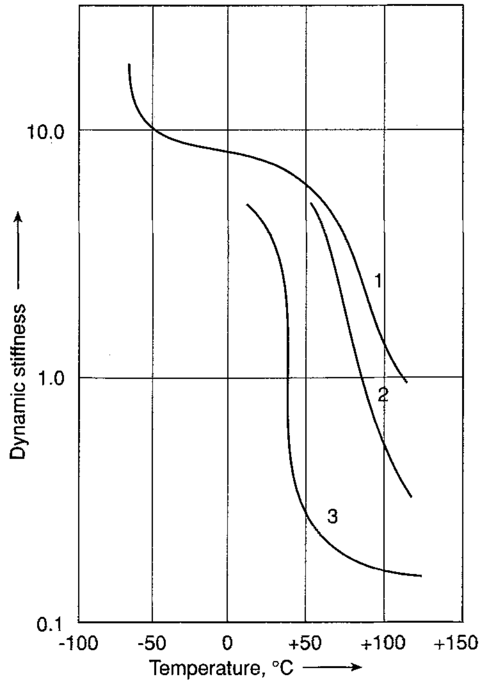


Figure 5.5 Effect of softening point of an aromatic resin on dynamic stiffness
1, 2, 3, as specified for Figure 5.4

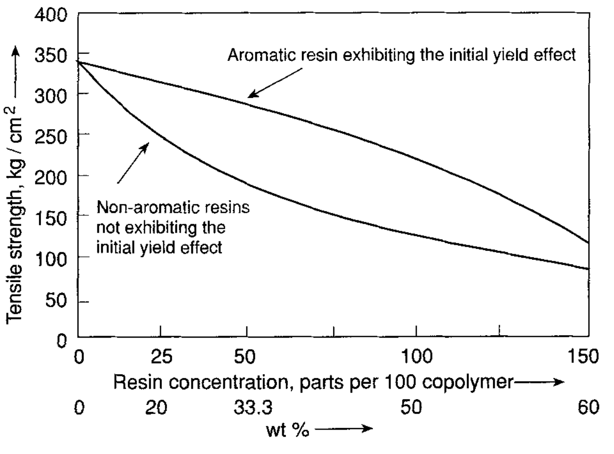


Figure 5.6 Tensile strength of SBS thermoplastic rubber/resin blends

Adhesives based on TR are of growing interest, especially because of their flexibility performance and their adhesion properties over a low to medium-high temperatur range. Their main application is in disposables, but they are also used in packaging and bookbinding.

A typical, oil-containing formulation comprises the following:

- Styrene block copolymer	30 %
- Tackifying resin	55 %
- Oil (e.g., naphthenic oil)	15 %
- Antioxidant	< 1 %

A proposed formulation for a hot-melt adhesive is:

- SBS block copolymer	100 parts
- C_4-modified C_9 resin, 100 °C R & B	150 phr
- Naphthenic oil	75 phr
- Stabilizer	6 phr

5.1.2.2.1 Diapers

This area is the largest outlet for TR-based hot-melt adhesives. Use is increasing because of their high flexibility and resistance to delamination. The main tackifiers used in this application are water-white resins. Pure aromatic, mixed terpene/styrene, or hydrogenated types may be used. To a lesser extent, rosin esters and C_5/C_9 resins are also employed.

5.1.2.2.2 Packaging

The main use is in plastic bottle fabrication (assembly) and in bottle labelling.

5.1.2.2.3 Bookbinding

TR-based hot-melts are of value in this application because of their good flexibility.

5.1.2.3 Polyolefin-Based Hot-Melt Adhesives

The polyolefins used as backbone polymers for hot-melts are polyethylene and polypropylene.

Polyethylene types typically have molecular mass 8000–10 000. Lower grades (molecular mass 1000–4000) may be added to reduce the softening point and melt viscosity. Higher molecular mass grades (10 000) may be added to increase toughness, softening point and viscosity.

Formulations are tackified with C_5, hydrogenated C_5, and terpene-phenol resins with softening points 100–130 °C R & B.

Polyethylene-based hot-melts are mainly used in packaging, carpet seaming, and disposables.

A typical formulation contains about 70 % polyethylene, 30 % tackifying resin, and 1 % antioxidant.

Uses in packaging include folding carton sealing, assembly of bags, and tray forming.

In diapers, polyethylene-based hot-melts are used in fine line lamination, but are increasingly being replaced by EVA- or TR-based hot-melts.

The polypropylene used for hot-melt adhesive formulation is atactic polypropylene (APP) with molecular mass 8000–10 000.

For use in bonding plies of Kraft paper and for cable filling, the natural tack is sufficient and no tackifying resin is added.

For use in packaging and other applications hydrogenated C_5 or terpene resins and wax are mostly added. A typical formulation is:

– APP	58 %
– Resin	25 %
– Wax	17 %

5.1.2.4 Heat Stability of Hot-Melts

As relatively high temperatures (up to 200 °C) are involved in hot-melt manufacture as well as in application, heat stability is very important. Heat and oxidation degrade color, viscosity, tack, and other properties of the final adhesive. Skinning may also occur.

Thus, the use of stabilizers is imperative, and this in the earliest stage of manufacture. Interaction between the hot-melt constituents or the influence of small impurities may become apparent under the influence of light and heat. Tackifying resins containing oxidation-sensitive structures, such as conjugated double bonds, tertiary carbon atoms, or allylic protons, may form peroxides, even at room temperature. Such resins must be stabilized in the production process.

In the following, some factors which influence thermal stability are discussed in some detail.

5.1.2.4.1 Influence of the Backbone Polymer

It has been found that the EVA type used has a very strong effect on the heat stability of the hot-melt. Generally, it can be said that the lower the melt index of the EVA type, the lower the heat stability of the finished system. Figure 5.7 shows this relation between heat stability and melt index.

The melt index indicates how many grams of the copolymer melt at a certain temperature in a time of 1 min. The diagram for an indene-rich C_9 resin demonstrates that increasing

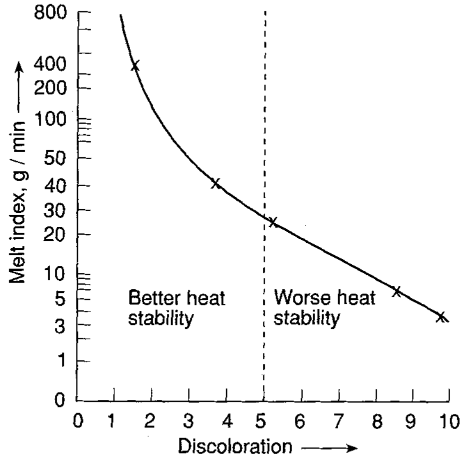


Figure 5.7 Heat stability of indene-coumarone and C_9 hydrocarbon resins in relation to the melt index of the EVA copolymer used

Test mixture: 33 % EVA copolymer, 33 % paraffin (drop point 60 °C), 1 % stabilizer, 33 % resin.

Evaluation (visual examination for degree of discoloration) is carried out after exposing the test mixture to a temperature of 180 °C for 48 h.

the melt index of the EVA improves the heat stability of the whole formulation. This applies generally, and does not depend on the type of C_9 resin used. The reduction of heat stability of the formulation with decreasing melt index cannot be prevented by adding an antioxidant.

5.1.2.4.2 Influence of Antioxidants (see also Sections 4.2.13 and 4.2.13.1)

The addition of antioxidants to hot-melt formulations is absolutely necessary; otherwise oxidative degradation of the polymers occurs, starting during production and continuing during storage of the hot-melt. Inappropriate or insufficient stabilization leads to discoloration, increase in reactivation energy of the finished hot-melt, and deterioration of physical properties such as thermal stability. It should be noted that most resin manufacturers stabilize all resins destined for hot-melt applications.

The tackifying resin should be stabilized as early as possible. Adding the stabilizer just after the final phase of the manufacturing process prevents peroxide formation, the first step in radical reaction which eventually leads to discoloration of the resin, degradation, and aging.

The selection of the appropriate stabilizer is important. Good results can be obtained by using stabilizer systems for their synergistic effect. Experience has shown that, for example, the following antioxidants, or similar types, in hot-melt formulations are particularly effective:

- 2,6-Di-*tert.*-butyl-p-cresol (BHT)
- Pentaerithrityl-tetrakis(3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)-propionate) or hydroxyhydrocinnamate
- Octadecyl-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)-propionate or hydroxyhydrocinnamate

BHT with its low molecular mass (220), is used as processing stabilizer. For long-term stabilization, compounds with higher molecular mass (above 300 and above 600) and low volatility, such as the hydroxy phenyl propionates, are suggested.

In block copolymers, the rubbery, unsaturated segments are very sensitive to oxidation. Protection by antioxidants is absolutely necessary. The most usual stabilizer is zinc-dibutyl-dithiocarbamate.

5.1.2.4.3 Effect of Fillers and Metal Salt Impurities

The main fillers in hot-melt adhesives are chalk (calcium carbonate), and barium sulfate. While chalk has no measurable effect on the heat stability of the hot-melt formulation, the various commercial barium sulfate types may show differences when used as fillers. These differences show in color degradation of the hot-melt during manufacture, as well as cracking at higher temperatures.

The tendency is for the differences to be more pronounced the more filler impurities are incorporated in the mixture.

It is known that traces of metal compounds catalyze the disintegration of polymers. This observation has also been made in hot-melt formulations. In particular, traces of copper

and chromium compounds may cause discoloration and degradation. They also considerably reduce the effectiveness of antioxidants. As an example, in a mixture of 0.5 % BHT in 4.5 g hot-melt formulation filled with barium sulfate, at a temperature of 150 °C, 40 % of the BHT is still detectable after 7 h. If the mixture contains 660 ppm copper, only 5 % BHT is detectable after 7 h.

Color deterioration due to the presence of 1000 ppm copper(I) oxide or chromic salts after 3 h at 150 °C is 2 units on the Barrett color scale.

The influence of metal ions is inhibited by addition of secondary stabilizers, e.g. tris-(nonylphenol) phosphite (TNPP). However, it should be used in combination with phenolic antioxidants.

The subject, in general, is so complex that the analytical investigation of impurities does not lead to any direct conclusions on the reactions of the filler in the formulation. However, an empirical method has been developed which permits the investigation of these reactions. The principle observed is that different hot-melt adhesives at a temperature of 250 °C show varying tendencies to swell. The expansion is caused by degradation (cracking) processes at this high temperature, accompanied by the splitting off of water. The evaporating water acts as a propellant and causes foaming. The expansion hight of the foam in a test tube is evaluated.

An expansion test formulation is:

- EVA 420	180 g
- Resin	50 g
- Chalk p.a.	25 g
- Barium sulfate	150 g

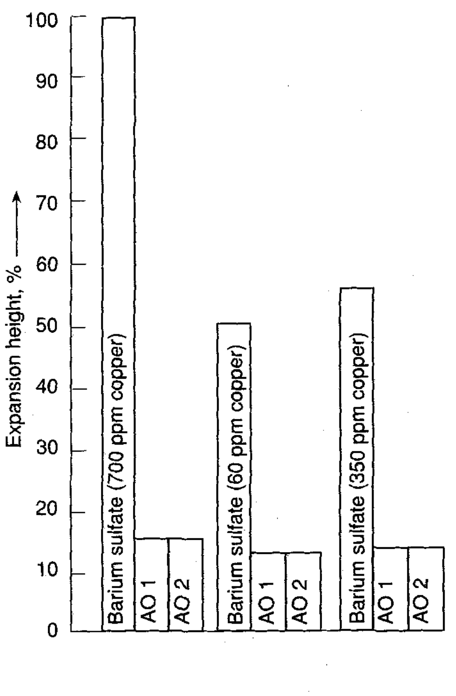


Figure 5.8 Effect of various grades of barium sulfate and stabilizers on the degradation of hot-melts

AO 1: addition of 0.3 % hydroxyphenylpropionate + BHT
AO 2: addition of 0.3 % hydroxyphenylpropionate + TNPP

The mixture is melted at 150 °C and kneaded for 1 h until it is homogeneous. Subsequently the mixture is kneaded for 1 h at 180 °C, and finally for 2 h at 200 °C. Subsequently, 5 g of the test material so prepared is transferred to a test tube and melted by heating to 250 °C within 3 min. The hight of filling in the test tube is then marked. The melt is then held for 15 min at 250 °C and the hight of the expanded material is marked for comparison with the original marking.

Figure 5.8 shows the effect of various barium sulfates and stabilizers on the degradation of hot-melts by comparison of the expansion hight. The differences between the individual barium sulfate types (with varying amounts of impurities) are clearly seen. However, all the barium sulfate types tested are usable with suitable stabilization.

This test is not only useful as a quality control for fillers, but is also applicable to each individual component of a hot-melt formulation.

5.1.3 Pressure-Sensitive Adhesives

A pressure-sensitive adhesive (PSA) is a viscoelastic material which, in solvent-free form, remains permanently tacky, and which will adhere instantaneously to most solid surfaces with a minimum of pressure.

Pressure-sensitive adhesives are mainly used in tape and label manufacturing. They are composed of a suitable backbone polymer, a tackifying resin, and a carrier (solvent, water) or may be applied by heating. Backbone polymers for PSA are elastomers, such as rubbers (natural rubber, SBR, block copolymers) and acrylics.

- Natural Rubber,

used in solvent-borne PSA is typically a premium grade pale crepe or smoked sheet having Mooney viscosity 55–65. To reduce the very high molecular mass, rubber has to be milled under well-controlled conditions to break it down. For water-borne formulations, a centrifuged type of natural rubber is used.

- Styrene-Butadiene Rubber (SBR)

is a heat-polymerized rubber with ca. 23 % of styrene and Mooney viscosity 45–60. Higher styrene-containing grades (40–45 %) may be added to improve mechanical properties. SBR latices normally contain 42 % of styrene and ca. 3 % of carboxyl groups.

- Block Copolymers,

suitable for PSA use are styrene-isoprene-styrene (SIS) and styrene-ethylene-butene-styrene (SEBS). SIS contains typically 14–21 % of styrene. The presence of olefinic unsaturation in the midblock makes it very sensitive to heat (see Section 5.1.2.4) and it has to be protected by antioxidants. It needs further protection under nitrogen during compounding and application. SEBS is a hydrogenated type (more expensive), possessing a saturated midblock and not sensitive to oxidation on heating.

- Acrylic Resins

are based on acrylate esters. For PSA applications, types with glass transition temperatures ca. -50 °C are used. Composition and molecular mass influence tack and mechanical properties. The large range available allows choice of well-adapted grades, normally needing no further formulation.

• Tackifiers
used in most formulations based on rubbers are:

- Aliphatic C_5 resins
- Aromatic C_9 resins and resins from pure monomers
- Polyterpene resins
- Hydrogenated resins
- Mixed C_5/C_9 resins
- Rosin and rosin esters

Choice of a particular resin depends on end use requirements, and is treated later in greater detail. In the following, some guidelines for selection based on the evaluation of viscoelastic properties of polymer/resin blends are given.

5.1.3.1 Permanent Tack and Viscoelasticity

Evaluation of suitability of resins for use in PSA normally involves expensive and time-consuming testing of tack, peel, and shear strength as the most important criteria. In fact, these properties are related to the basic rheological properties of an adhesive.

It is generally accepted that viscoelastic properties give evidence of the mechanism of tackification. Important research has been carried out in this field by workers from Hercules Inc., mainly S.G. Chu, J.B. Class and co-workers [5.7-5.10].

They have evaluated the influence of resin structure, molecular mass and resin concentration in blends with natural rubber, SBR, and thermoplastic rubber by studying viscoelastic properties such as G', the relaxation modulus (ratio of stress to corresponding strain, time dependent), and where $\tan \delta = G''/G'$; G'' = shear loss modulus, G' = shear storage modulus. It is beyond the scope of this chapter to go deeper into these considerations. Further information is available in more specialized literature, e.g., [5.11].

According to S.G. Chu and J.B. Class, compatibility of tackifying resins with elastomers depends on structure and molecular mass, thus affecting viscoelastic properties, and is strongly related to the performance of the pressure-sensitive adhesives.

Figure 5.9 gives guidelines for making PSA [5.12].

Further details are beyong the scope of this book, and the reader is referred to the original literature [5.7-5.11]. A few examples and a simplified description are given below. Compatibility, and hence the suitability of a resin for use as tackifier for a PSA in a given particular system may be evaluated by comparing the G' and $\tan \delta$ values, plotted against temperature, for the backbone polymer and its mixture with a given resin.

Compatibility is indicated if the $\tan \delta$ peak is significantly shifted to higher temperature, and if G' for the rubbery plateau is reduced (Fig. 5.10).

Incompatibility, on the other hand, is shown by little or no shift of the $\tan \delta$ peak, and the appearance of a second peak at higher temperature, attributed to a second phase which is predominantly resin. Also, G' is increased for the rubbery plateau.

Block copolymers, because of their special structure, i.e., rigid aromatic endblocks and rubbery aliphatic midblocks, have two glass transition temperatures, one for each of

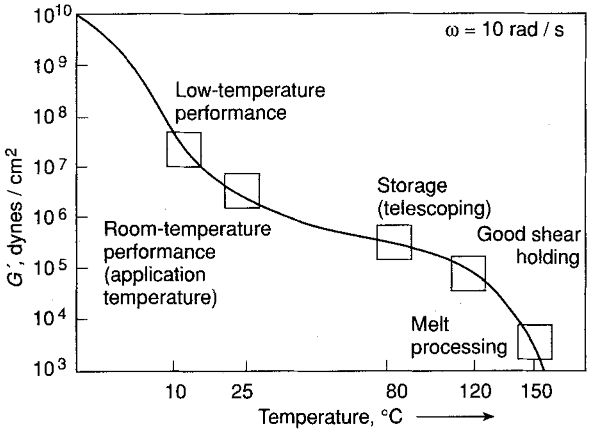


Figure 5.9 Guidelines for making pressure-sensitive adhesives shown as "windows" of performance

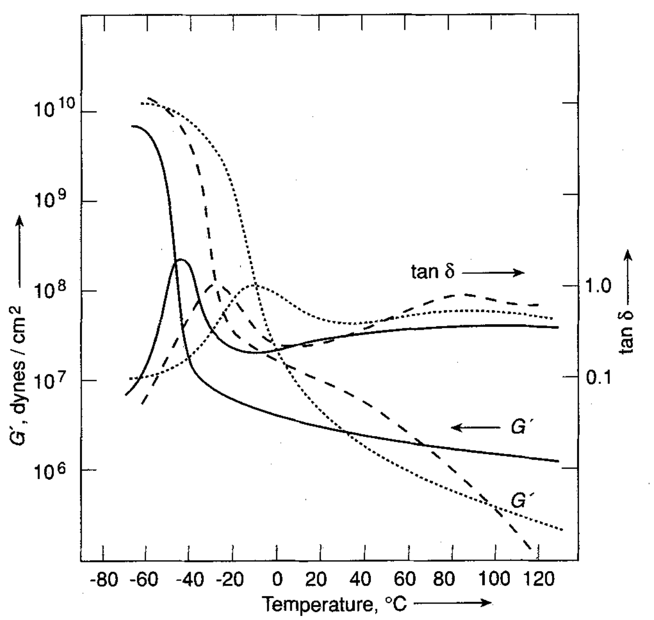


Figure 5.10 Influence of resin structure on compatibility

1:1 blend of SBR with

a poly(vinylcyclohexane) resin, $\overline{M}_w = 650$, $\overline{M}_w/\overline{M}_n = 1.4$ → -----

a polystyrene resin, $\overline{M}_w = 900$, $\overline{M}_w/\overline{M}_n = 1.6$ → ......

SBR → ———

the immiscible phases. Mixtures of tackifying resins are used, including types which associate with the rubbery midblock (aliphatic resins) and types which reinforce the glassy endblock (aromatic resins).
The influence of tackifiers on the backbone polymer can be observed by comparison of the dynamic mechanical properties of the basic polymer and its mixtures with resins. J.B. Class [5.10] describes studies involving comparison of such features as the temperature of the tan δ peak (which is associated with the glass transition temperature), G' at the temperature where tan δ reaches a minimum in the rubbery plateau (which is an approximation of the plateau modulus), and the temperature where G' and G'' (tan δ =1) at the high-temperature end of the plateau (which signifies the onset of terminal flow).

Dynamic measurements of viscoeleastic data give the following results: Midblock-compatible resins (mainly aliphatic) increase the tan δ peak temperature and reduce plateau modulus. They also reduce the temperature of onset of terminal flow. This may result from a concentration reduction of the endblock phase, and from dilution of the entanglement network at elevated temperature.

A midbloc-incompatible resin (aromatic) does not affect the tan δ peak temperature, but induces an increase in the plateau modulus of SBS and SEBS thermoplastic rubber. With SIS-TR, however, the aromatic resin seems to be partially compatible, but appears to reduce the plateau modulus slightly.

The aromatic resin does not influence the G' and G'' transition temperature of SEBS and SIS-TR at the concentrations studied. It raises the temperature for SIS and lowers that for SBS.

Uses for pressure-sensitive adhesives include tapes, labels, and decalcomania. The largest quantities go into tape production. Several hundred types are produced, designed for specific applications, varying in type of backing and adhesive. Only the most important applications are considered here.

5.1.3.2 Tapes

Paper tapes are commonly used in packaging and temporary protection during painting, polypropylene tapes in packaging, acetate and cellophane-based tapes for stationary, pipe wrapping, PVC for electrical insulation, etc.

• Paper tapes use mainly natural rubber and polyisoprene-based adhesives, as well as SIS solutions. A typical formulation (parts per weight) is:

- Natural rubber	100
- Tackifier (C_5 resin or C_5/ rosin ester)	100
- Filler	50
- Antioxidant	2
- Solvent (hexane)	500

Formulations based on SIS solutions contain less solvent, about 55 % instead of 65 % for the above formulation.

• Polyethylene tapes are used for pipe wrapping. A typical formulation is:

– Butyl rubber	40 %
– Polybutene	10 %
– Aliphatic C_5 resin	15 %
– Fillers	35 %

• Duct tapes are normally based on polyethylene-coated cotton cloth. The adhesive formulation contains natural rubber, tackifier, filler, and antioxidant and is calendered on the substrate. For example:

– Natural rubber	40 %
– C_5 resin	40 %
– Filler (calcium carbonate)	19 %
– Antioxidant	1 %

• Polypropylene tape, used for packaging may use hot-melt (more than 50 %) or acrylic emulsions as adhesive. A hot-melt formulation is given below:

– SIS block copolymer	34–40 %
– C_5 resin	50–55 %
– Naphthenic oil	10 %
– Antioxidant	0.5–1 %

• PVC tapes for electrical insulation and for packaging make use of essentially rubber-based adhesives.

• Polyester tapes are mainly used in packaging. Adhesives are made with natural rubber and SIS in solution; some acrylics and SIS hot-melts are also used.

• Acetate- and cellophane-backed tapes are used essentially in office stationary. The first type uses acrylic emulsions, and to a less extent, acrylic solutions. The second type uses natural rubber or synthetic polyisoprene solutions.

There are also many other specialized tapes, but they are not very different from these examples and are not discussed here.

• Medical tapes: There are many different medical tapes. They are based on different backings and adhesives, mainly SIS hot-melts and to a lesser extent natural rubber. Requirements for these applications include skin compatibility, and careful selection of formulation ingredients is necessary. An example of a possible formulation is:

– Natural rubber	ca. 30 %
– Tackifier (rosin esters)	ca. 30 %
– Fillers	ca. 20 %
– Anti-inflammatories	ca. 20 %
– Antioxidant	1–1.5 %

5.1.3.3 Labels and Decalcomania

Labels and decalcomania applications form the second major area for pressure-sensitive adhesives. Backings may be multiple: paper and plastics such as polyester, PVC, polycarbonate, and other special materials.

Adhesives for paper labels are based on SIS hot-melts, SBR/natural rubber emulsions, acrylic emulsions, SBR and polyisobutene solutions. Acrylic solutions are mainly used for plastic labels and decals.

• Paper labels are a combination of an adhesive-coated paper and a silicon-coated release liner. They are available as permanent, removable, and freezer labels. Permanent labels account for the largest volume. Adhesives are SIS hot-melts, SBR latex and solutions. A typical formulation is:

– SIS	35 %
– Aliphatic C_5 resin	50 %
– Naphthenic oil	14 %
– Antioxidant	0.5–1 %

• Removable labels utilize polyisobutene and acrylic emulsions. A typical formulation (parts by weight) is:

– High molecular mass polyisobutene	100
– C_5 resin, high softening point	45–50
– Liquid rosin ester	25–30
– Polybutene plasticizer	50–70
– Antioxidant	0.5
– Hexane	to 25 % solids

• Freezer labels use the same adhesive systems. Plastic label and decal adhesives are mainly based on acrylic solutions.

It should be noted that C_9 resins of the liquid or semiliquid type are sometimes used, together with other hydrocarbon resins to adjust their properties (for instance viscosity). Suggested types are liquid or semiliquid C_9 resins rich in α-methylstyrene/vinyltoluene.

5.2 Sealants

Sealants used in various applications are based on polymers such as butyl rubber, polyisobutene, polybutene, thermoplastic elastomers, SBR, neoprene, and polysulfide polymers. These polymers need the addition of tackifying resins to improve instantenuous adhesion. Silicones, urethanes, and similar materials are applied as low molecular mass "prepolymers" and do not need added tack. Sometimes adhesion promoters or surface primers may be used.

Tackifiers for these polymers are:

- Polybutene
- C_5 aliphatic hydrocarbon resins
- Hydrogenated dicyclopentadiene resins
- Polyterpene resins
- C_9 aromatic hydrocarbon resins
- Indene-coumarone resins

- Resins from pure monomers
- Modified and unmodified rosin
- Nonreactive phenolic resins
- Gilsonite

The main criteria for tackifier selection are compatibility with the backbone polymer, softening point, color (for some applications), weathering stability, thermal stability, approval for food applications, and price.

Sealants are widely used in construction, glass insulation, the automotive industry, and various other areas.

Sealants based on butyl, polyisobutene, and ethylene-propylene rubber are formulated with liquid polybutene as extender, plasticizer, and tackifier. Sometimes an aliphatic tackifying resin is also added. The formulation also contains fillers. Butyl rubber may be cross-linked with sulfur or other curing systems. These sealant types may be used as tapes, hot-melts, or caulks. Some basic examples for starting formulations are:

• For tapes:	– Polyisobutene	20–30 %
	– Polybutene	20–30 %
	– Fillers	45–60 %
• Hot-melts:	– Butyl rubber (partially cross linked)	30–50 %
	– Polyisobutene	5–20 %
	– Tackifying resin	1–30 %
	– Fillers	10–30 %
	– Polybutene	0–20 %

Sealants based on bitumen or similar material may be modified with butyl rubber and contain polybutene, a C_5, C_9, or indene-coumarone resin, together with fillers.

Styrene block copolymers for sealant use are formulated with tackifying resins (aliphatic midblock-associating and aromatic endblock-associating resins) and solvent, or without solvent as hot-melts.

Liquid polysulfide polymers are used to produce high-grade sealants. This involves one- or two-pack systems having excellent rubber-like stress/strain properties, combined with good adhesion to wood, cement, aluminum, etc. The manufacture of flexible sealants using different types of polysulfide polymers leads to the use of a number of application techniques, e. g., casting, filling, coating, spraying.

In the formulations of sealants, the main components are:

- Polysulfide polymers
- Plasticizer
- Filler
- Hardener

By changing the quantity ratios of the main components, the system can be formulated to meet specific requirements. Changes in quantity ratio in many cases allows for cost saving. One of the most important properties of a sealant is its adhesion to the substrate. On this basis, selected hydrocarbon resins are added to improve the adhesion properties in sealants and similar systems based on polysulfide polymers. Nonreactive liquid C_9 hydrocarbon resins have proved to be of interest. Recent developments have shown that reactive special

liquid resins perform even better as adhesion promoters. It is self-evident that the quantity of the added special liquid resin depends on the specific performance requirements of the polysulfide system. The special liquid resin types do not influence the cure hardening. Sealants retain relatively low elastic modulus, and good adhesion when manganese dioxide is combined as a hardener. The maximum quantity of added liquid resin as an adhesion promoter depends on the individual end formulation.

The following gives a general guideline for the formulation (parts per weight) of a sealant for cement (without primer):

• **Composition**	– Polysulfide polymer	100
	– Special liquid resin	10
	– Phthalate plasticizer	45
	– Filler (chalk, kaolin, etc.) and pigments (TiO_2)	85
• **Hardener**	– Manganese dioxide	8
	– Phthalate plasticizer	8
	– Accelerator	0.5

Cable insulation oils and sealants are normally based on mineral oils and aromatic C_9 or indene-coumarone resins. Mineral oils may be mixtures of naphthenic and paraffinic oils with at least 50 % of naphthenic oil to assure good compatibility with the aromatic resin.

• **A typical formulation** (parts by weight) is:

– Aromatic solvent	15–20
– Paraffinic oil	35–50
– Naphthenic oil	50
– Aromatic petroleum-based or indene-coumarone resin	10–45

• **Viscosity:** 290 cSt (+10/–30) at 70 °C; 25 cSt at 120 °C

Owing to their good dielectric properties, the neutral and unsaponifiable IC and C_9 resins have found applications in the electrical industry as insulating materials, as components for cable insulating oils or sealing compounds, and as impregnating and potting compounds. For application in these fields, the availability of resins with uniform electrical data, true to specifications, is indispensable. The most important electrical data, the relative dielectric constant and the loss factor of aromatic hydrocarbon resins must lie within a suitable range. Other electric data, such as specific resistance and dielectric strength are in accordance with the requirements for insulating materials. Detailed values are available from resin producers.

5.3 Coatings

Coatings cover a large field of applications, from protective to decorating coatings, for temporary or permanent use. The main uses for hydrocarbon resins are in packaging, paints, overprinting, curing membranes, road markings, roof and pipe coatings, automotive and truck undercoatings.

5.3.1 Hot-Melt Coatings

Hot-melt coatings are widely used in the packaging industry, mainly for food packaging: cardboard boxes for milk and fruit juices, waxed papers, and many similar applications.

The packaging industry uses molten wax, wax blends (often with EVA or hydrocarbon resins), polyolefins, or hot-melt coatings formulated with EVA, tackifying resins, and waxes. They may be applied by curtain coating, impregnation or roll-coating.

The most important functions of those coatings are moisture resistance and barrier properties to prevent moisture/vapor transfer between packed goods and the surrounding. All ingredients in food packaging must be approved for this application. Paraffin waxes are used, a macrocrystalline wax and a more flexible microcrystalline wax. Mixtures to optimize properties and price are often used. Modification of waxes by EVA allows one to improve properties such as adhesion, flexibility, hardness, and strength. EVA grades with ca. 20 % of vinyl acetate are currently used.

Resins enhancing wax/EVA compatibility, water repellency, and adhesion for these applications are mostly the higher-priced types, with low odor, low color, and approval for use in food applications. Examples include synthetic polyterpene resins (piperylene-type C_5 resins), standard polyterpene resins, rosin esters, and some aromatic monomer-based resins. In non-food applications or overpackaging, aromatic C_9 or aliphatic-modified C_9 resins are also used. Formulations may contain the following quantities:

– Paraffin wax	50–75 %
– Microcrystalline wax	15–30 %
– Polyethylene	0–20 %
– EVA	2–20 %
– Resin	5–15 %

Thermoplastic road marking is used for special applications. In comparison with the usual alkyd-based traffic paints, both drying time and lifetime are improved.

The binder system is mostly a mixture of resins, e. g., rosin esters and C_5 or dicyclopentadiene resins (15–20 %), white pigment (TiO_2, ca. 25 %), filler ($CaCO_3$, 45–50 %) and reflective glass beads (ca. 25 %). Film thickness is about 2–3 mm when coated normally, and ca. 5–7 mm when screen-applied into flat recesses. For yellow markings aromatic resins may also be used, but when unstabilized they are more sensitive to oxidation and discoloration.

5.3.2 Paints and Varnishes

Binders for the varnish and coatings industry often contain so-called hard resins. These resins are added:

- to improve film hardness
- to enhance gloss and gloss retention
- to shorten drying time in air-drying systems
- to improve adhesion to the substrate
- to improve water repellency and resistance to acids and alkalis

Classically, these resins are rosin derivatives and hydrocarbon resins of aromatic, aliphatic, or dicyclopentadiene type. They may be used as the sole or predominant binder, e. g., in aluminum paints, or together with basic binders such as drying oils and alkyd resins and various other binder types.

Reactive hydrocarbon resins, e. g., the unsaturated DCPD resins, may be cooked with drying oils or reacted with maleic anhydride to form new binder types.

Resins with softening points 100–120 °C R & B are mainly used in the formulation of aluminum and bronze paints, primers, temporary coatings, and alkyd paints.

For use in paint systems, the solubility in normal paint solvents and compatibility with various basic binders are important.

- **Solubility:**

Typical C_9 resins are readily soluble in esters, ketones, aromatics, chlorinated hydrocarbons, ethers, and white spirit (aromatic content 15–18 %). Further solubility can be achieved by adding glycol, glycol esters, and glycol ethers. C_5 resin types are also soluble in pure aliphatics.

Apart from a few exceptions, e. g., methoxypropanol and 2-isopropoxypropanol, in which some C_9 resin types are partly or totally soluble, alcohols in general are not suitable solvents. Extremely good solubility is achieved in terpene-type solvents (pine oil, dipentene, turpentine oil).

Solubility characteristics in normal solvents for a typical C_9 and a phenol-modified C_9 resin with softening points 100 and 120 °C R & B are given in Table 5.3 [5.13].

Table 5.3 Solubility of resins

	C_9 Resins		Phenol-modified C_9 resin	
Softening point, °C R & B:	100	120	100	120
Alcohols:				
Methanol	is	is	is	is
Ethanol	is	is	is	is
Isopropyl alcohol	is	is	is	is
Butanol	is	is	is	is
Methoxypropanol	is	is	is	is
Methoxybutanol	is	is	is	is
Diacetonalcohol	is	is	is	is
Isopropoxypropanol-2	s	s	ps	ps
Esters:				
Methyl acetate	s	s	s	s
Ethyl acetate	s	s	s	s
Butyl acetate	s	s	s	s
Methoxypropyl acetate	s	s	s	s
Methoxybutyl acetate	s	s	s	s

Table 5.3 (continued)

	C_9 Resins		Phenol-modified C_9 resin	
Softening point, °C R & B:	100	120	100	120
Glycol alcohols:				
Methy glycol alcohol	s	s	ps	ps
Ethyl glycol alcohol	s	s	s	ps
Butyl glycol alcohol	s	s	s	s
Glycol esters:				
Methyl glycol ester	ps	is	ps	ps
Ethyl glycol ester	s	s	s	s
Butyl glycol ester	s	s	s	s
Glycol ether:				
Dipropylene glycol monoisopropyl ether	ps	ps	s	s
Ethers:				
Tetrahydrofuran	ps	ps	is	is
Methyl tetrahydropyran	s	s	s	s
Ketones:				
Acetone	is	is	ps	ps
Methyl ethyl ketone	s	s	s	s
Methyl isobutyl ketone	s	s	s	s
Cyclohexanone	s	s	s	s
Isophorone	s	s	s	s
Acetophenone	s	s	s	s

Table 5.3 (continued)

Softening point, °C R & B:	C_9 Resins 100	120	Phenol-modified C_9 resin 100	120
Aromatics:				
Aklylbenzenes:				
Toluene	s	s	s	s
Xylene	s	s	s	s
Solvent 100	s	s	s	s
Solvent 150	s	s	s	s
Aromatic mixtures:				
Solvent naphtha	s	s	s	s
Hydronaphthalenes:				
Tetraline	s	s	s	s
Decaline	s	s	s	s
Aliphatics:				
Dearomatized aliphatics:				
b. p. 100/140	s	s	s	s
b. p. 150/195	s	s	s	s
Isoparaffins:				
b. p. 116/144	ps	ps	is	is
b. p. 155/174	ps	ps	is	is
Chlorinated hydrocarbons:				
Trichloroethylene	s	s	s	s
Carbon tetrachloride	s	s	s	s

Table 5.3 (continued)

Softening point, °C R & B:	C_9 Resins 100	120	Phenol-modified C_9 resin 100	120
Terpenes:				
Pine oil	s	s	s	s
Dipentene	s	s	s	s
Citrus terpenes (limonene)	s	s	s	s
Miscellaneous solvents:				
Butylketole	ps	ps	s	s
2-Methylpyrrolidone	ps	ps	s	s
Propylene carbonate	is	is	is	is
Methyl isobutyl carbinole	is	is	is	is

The solubility data refers to temperature 16–24 °C.
s = solution in each type of concentration is clear, dried film is clear

ps = solution clear or slightly cloudy; during drying, film is temporarily cloudy, but after complete evaporation of solvent it becomes clear again

is = solution is cloudy or inhomogenous in all types of concentrations (particles become swollen or oxidized white, also phase separation and slimy precipitate).

Because of their usually ligh solubility, hydrocarbon resins reduce the viscosity of paint formulations, thus allowing markedly higher solids content and reduction of solvent emissions.

- **Compatibility:**

  Most hydrocarbon resins show good compatibility with a wide range of other binder types used in formulating paint systems. Some of the most important combinations are briefly discussed below:

  Drying and non-drying oils, with the exception of high-viscosity stand oils, can be combined with hydrocarbon resins. Cooking for long periods at a critical temperature of 285 °C does not result in gelling. In oil/hydrocarbon resin cooking, manganese drying agents should be avoided. Addition of antioxidants to prevent skinning is not necessary.

  Hydrocarbon resins may be combined with alkyd resins. They exhibit good compatibility with many types, including acrylic- and styrene-modified alkyds, and with some limitations also with epoxy-modified alkyds. The combination of hydrocarbon resins with drying oils and alkyds in the formulation of industrial corrosion protection and wall paints is one of the main areas of application. Some examples of the compatibility characteristic of hydrocarbon resins with these binder types are given in Table 5.4 [5.14].

Tabel 5.4 Compatibility of drying oils and alkyd resins with C_9 resins

Softening point, °C R & B	100		120	
Resin/oil or alkyd resin	50/50	25/75	50/50	25/75
Oils:				
Linseed oil	pc	c	c	c
Linseed stand oil (60 P)	c	c	c	c
Tall oil	c	c	c	c
Long-oil alkyd resins:				
Linseed oil based	c	c	c	c
Tall oil based	c	c	c	c
Medium-oil alkyd resins:				
Linseed oil based	c	c	ic	pc
Tall oil based	pc	c	pc	c
Short-oil alkyd resins:				
Linseed oil based	ic	pc	ic	pc
Fish oil based	ic	c	ic	ic

c = totally compatible; pc = partially compatible; ic = incompatible

It should be noted that phenol-modified C_9 resins exhibit a markedly wider compatibility with these combination partners than straight C_9 resins.

Modified natural resins are mostly highly compatible with all hydrocarbon resins, including all colophonium derivatives, such as rosin esters, phenol-modified colophonium resins, and similar components.

Polycondensation resins include ketone resins, formaldehyde resins, and carbamide resins as representatives of the so-called hard resin types; they are compatible with hydrocarbon resins. There is no compatibility with aminoplast and melamine resins.

Combination of **polyacrylates** with hydrocarbon resins is possible. Some types are also suitable for combination with **polyvinylether** and vinylchloride/vinylisobutyl ether copolymers. Combinations with **co- and ter-polymerisates** in the area of styrene, butadiene, acrylate, vinyl chloride, acrylonitrile, offer further interesting possibilities. In this case, and in similar combinations, the solids content can be increased by the addition of hydrocarbon resins, because in most cases they reduce the solvent viscosity of the system.

Elastomers are often blended with hydrocarbon resins. Chlorinated rubber, for instance, widely used in many paint systems, is an excellent combination partner. Polybutadiene and polychlorobutadiene are also suitable for combination. Here, too, blending with hydrocarbon resins allows a high solids content and has an advantageous effect on processing. Polybutene and polyisobutene are not compatible with aromatic hydrocarbon resins.

Epoxy resins with an epoxy equivalent of 175–210, and even epoxy resin esters, are compatible with many petroleum resin types. Phenoxy resin formulations can be modified

by addition of hydrocarbon resins. In this and similar cases, a price advantage is also achieved.

It should be pointed out that the most suitable modification resins, also acting as extenders, are the light-colored, solvent-free, special liquid resins. They are available commercially as neutral standard types and as activated types with an OH number (see also Section 5.3.5).

In the group of **cellulose derivatives** only phenol-modified C_9 resins exhibit limited compatibility, e. g. with cellulose nitrate. This facilitates partial replacement of these derivatives in various nitro varnish formulations.

It should also be mentioned that hydrocarbon resins are compatible with nearly all standard **plasticizers**.

5.3.2.1 Aluminum Paints

Aluminum finishings are used as coatings for tanks, silos, containers of all types, as well as for bituminous roofs, where they are appreciated for their high reflection power for heat and light. The binders for aluminum paints have a strong influence on the leafing properties and the leafing stability of the systems. It is known that binder materials having zero or very low acid number are very well suitable for the formulation of aluminum paints with leafing and storing stability. These conditions are fully met by indene-coumarone and petroleum-based hydrocarbon resins. They are absolutely neutral, unsaponifiable, water-free, and they normally have an acid number < 0.1 %. Binders with higher acid number and higher polarity are less well suited. When using resins, care should be taken that the resins have not been stored for too long. Depending on the particle size, stability, and degree of exposure to air and light, the oxidative influence of atmospheric oxygen becomes noticeable on prolonged storage. This leads to a slow unwanted increase of the acid number. In oxidative drying systems, lead, manganese, zinc, and calcium are to be avoided to exclude the danger of greying of aluminum paint. Cobalt driers are suggested instead.

Depending on the degree of fineness of the aluminum powder, approximately 12–16 % of commercial aluminum pastes (65 %) are used for interial paints and about 20 % for heat- and weather-resistant paints.

To incorporate the aluminum pastes in the lacquer, predispersion of the aluminum component in the selected solvent system in the ratio 1 : 1 (up to 1 : 2) is suggested as the first processing step. At this point, short-term application of a low-speed mixer is suggested in order to avoid increased mechanical stress, otherwise abrasion of the fatty acid stearate protective coating of the aluminum particles may occur, with the generally negative effects known. It is also possible to add the solvent to the aluminum paste slowly in small portions during slow stirring.

Selection of the solvent is also of importance. For instance, white spirit, toluene, xylene, solvent naphtha, decalin, or tetralin can be used, as these solvents have no negative effect on the leafing properties of the aluminum. A low viscosity of the aluminum lacquer and a partial content of aromatic solvents in the lacquer systems markedly enhance the leafing properties of the aluminum powders and give the system a silvery gloss. Chlorinated hydrocarbons should not be considered, as according to the information from

the manufacturers of aluminum pastes, a reaction with the finely dispersed aluminum may occur. After the predispersion process, the dissolved binder material (high dilution) is then blended slowly under continuous stirring with the aluminum paste pretreated as outlined above. By the special dispersion process described above, attack on the laminar structure or the above mentioned surface coating of the aluminum pigments can be avoided.

Absence of water in all components used in the formulation of aluminum paints is also of importance as the presence of water can lead to production of hydrogen and hence to an increase of pressure in closed containers. The addition of various paint additives depends on the compatibility with the aluminum pigment and is to be tested in each case (reference is made to the corresponding guide books of the aluminum paste manufacturers).

In the so-called non-leafing aluminum paints, indene-coumarone resins and C_9 hydrocarbon resins can also be used as binder materials. An impairment in the quality of the aluminum pigments is not to be expected. In formulating gold colors/gold bronze paints, indene-coumarone and hydrocarbon resins are also suitable binders. Here, too, it is important that the binder materials are neutral and that they have zero or very low acid numbers.

The following formulations using indene-coumarone and C_9 hydrocarbon resins as binder, should give a lead for formulating aluminum paints for various stress and areas of application.

Aluminum paints by cold-blending:

- Low-Priced aluminum paint for general application

– Aluminum paste (65 % Al powder)	15 %
– Indene-coumarone or C_9 resin (preferably with high indene-content, 120 °C R & B)	14 %
– Mineral spirit	47 %
– Aromatic solvent	22 %
– Tetralin	2 %

- Heat-resistant aluminum paint

– Aluminum paste (65 % Al powder)	27.5 %
– Indene-coumarone or C_9 resin (preferably with high indene-content, 120 °C R & B)	16 %
– Mineral spirit	34 %
– Aromatic solvent	20 %
– Tetralin	2.5 %

- Weather-resistant aluminum paint

	First-finishing	Second-finishing
– Aluminum paste	15 %	20 %
– C_9 resin (preferably with high indene content, 120 °C R & B)	12 %	10 %
– Dehydrated castor stand oil (60 P)	30 %	32 %
– Mineral spirit	25 %	23 %
– Aromatic solvent	15 %	12.5 %
– Tetralin	2 %	2.5 %
– Cobalt naphthenate (6 % Co)	0.3 %	0.45 %

- Chlorinated rubber-based aluminum paint, quick drying

– Aluminum paste (65 % Al powder)	12 %
– Chloroparaffin 40	8 %
– Chlorinated rubber	10 %
– C_9 resin (preferably with high α-methylstyrene/vinyltoluene content, 120 °C R & B).	20 %
– Aromatic solvent	50 %

Aluminum paints prepared by cooking:

In cooked systems, standard C_9 resins or C_9 resins with a high α-methylstyrene/vinyltoluene content are preferred as their solubility in white spirit is better compared with indenes-coumarone resins and C_9 resins with a high indene content which normally perform well in cold-blended systems. If indene-coumarone resins are used, aromatics have to be added to the solvent, as otherwise strong flocculation may occur. As this phenomenon is not observed when using standard C_9 or low-indene C_9 resins, C_9 resins with a high α-methylstyrene/vinyltoluene content are preferred when using white spirit without a higher aromatics content. Nevertheless, the addition of some aromatics is recommended, which results in a lower viscosity, so that leafing of the aluminum powder is supported.

General standard aluminum paints:

C_9 resin*	28 %	Indene-coumarone resin (120 °C R & B)	29 %
Linseed stand oil (600 P)	22 %	Linseed stand oil (50 P)	16 %
Mineral spirit	50 %	Mineral spirit	45 %
		Xylene	10 %
Cobalt naphthenate (6 % Co)	0.18 %	Cobalt naphthenate (6 % Co)	0.13 %

(* standard C_9 resin or C_9 resin with high α-methylindene/vinyltoluene content; 120 °C R & B)

Resin and oil are cooked together at 280 °C. After cooling, solvents and drier are added.

C_9 resin*	13 %	Indene-coumarone resin (110 °C R & B)	13 %
Bodied linseed/wood oil (80/20; 90 P)	37 %	Linseed stand oil (90 P)	27 %
Xylene	10 %	Xylene	10 %
Mineral spirit	40 %	Mineral spirit	50 %
Cobalt napthenate (6 % Co)	0.4 %	Cobalt naphtenate (6 %Co)	0.15 %

(* standard C_9 resin or C_9 resin with high α-methylstyrene/vinyltoluene content; 120 °C R & B)

Resin and oil are cooked together at 280 °C. After cooling, solvents and drier are added

5.3.2.2 Alkyd Paints

The basic binder systems in alkyd paints may be modified with aromatic hydrocarbon resins to improve gloss and film-forming properties, water, acid, and alkali resistance. Another advantage is the viscosity lowering effect, allowing formulations with high solids content and considerable body. Replacement of ca. 20 % of alkyd resins by hydrocarbon resin is recommended. Some formulation possibilities are given below [5.15]

- Exterior gloss white paint

– Linoleic acid-based alkyd resin, long-oil type (75 % solids)	38 %
– C_9 resin*	8 %
– Titanium dioxide	26 %
– Calcium carbonate	11 %
– White spirit	15 %
– Drier	2.2 %
– Anti-skinning agent	0.4 %

(* preferably with high α-methylstyrene/vinyltoluene content; 120 °C R & B)

- Rapid drying alkyd enamel

– Medium-oil alkyd resin (70 % solids, special non-yellowing type)	43 %
– C_9 resin*	4 %
– Titanium dioxide	33 %
– Xylene	18 %
– Drier	2.2 %
– Anti-skinning agent	0.4 %

(* preferably with high α-methylstyrene/vinyltoluene content; 120 °C R & B)

- Anticorrosion paint

– C_9 resin*	22.5 %
– Medium-oil alkyd resin (50 % solids, fish oil based)	5.0 %
– White spirit (17/18 % aromatics)	22.5 %
– Calcium carbonate	25.0 %
– Kaolin	6.25 %
– Red iron oxide (Fe_2O_3)	18.75 %
– Drier	0.2 %

(* preferably with a high α-methylstyrene/vinyltoluene content; 120 °C R & B)

5.3.2.3 Miscellaneous Paint Types

Various other polymers used as binders in the paint industry, such as polyisobutyl acrylate, styrene-butadiene elastomers, polyvinyl isobutyl ether, vinyltoluene-acrylate copolymers, may be modified with hydrocarbon resins. Some formulations are given below:

- Clear aliphatic solvent-based varnish

– Polyisobutyl acrylate	28 wt %
– C_9 resin, low indene content, 100 °C R & B	5 wt %
– Isoparaffin solvent 116/144	40 wt %
– Isoparaffin solvent 155/174	20 wt %
– Methoxypropyl acetate (MPA)	10 wt %

Polyisobutyl acrylate and the hydrocarbon resin are separately dissolved in isoparaffin. On mixing, an emulsion is formed, which after addition of MPA becomes clear. Viscosity may be adjusted.

- Varnishes with increased water resistance

- Elastomer based on styrene-butadiene	20 wt %
- Toluene	20 wt %
- C_9 resin, low indene content, 110 °C R & B	5 wt %
- Aromatic solvent naphtha	55 wt %
- Vinyltoluene-acrylate copolymer	25 wt %
- C_9 resin, low indene content, 100 °C R & B	5 wt %
- Aromatic solvent naphtha 100	45 wt %
- Aliphatic solvent naphtha 140/170	20 wt %
- Chloroparaffin	5 wt %

The resin content can be increased or decreased in all these formulations, depending on the intended properties regarding weather resistance and flexibility.

5.3.2.4 Road-Marking Paints

For road markings, paints are used more than thermoplastic materials (see Section 5.3.1). The coating thickness is ca. 0.5 mm. These paints are based on binder systems containing alkyd resins, SBR, or chlorinated rubber, combined with hydrocarbon resins or rosin esters. The main requirements are stability to light and abrasion resistance.

Resin characteristics must meet the following standards: light stability (UV resistance), neutral and unsaponifiable, resistant against water, diluted acids, alkali, and mineral oils, good film-forming and wetting properties, good compatibility with synthetic rubbers, synthetic copolymers, and other resins which are normally used in the formulation of road-marking systems. Good thermal stability allows heating to temperatures of ca. 200 °C.

For this area of application, there are a number of commercially available resins, especially low-priced binders. The aliphatic C_5 resin types are by far the most popular, but other resin types are also used:

- C_5 (DCPD)-modified C_9 hydrocarbon resins
- Hydrogenated hydrocarbon resins
- C_4-modified C_9 hydrocarbon resins
- C_9 resins with low indene and high α-methylstyrene/vinyltoluene content.

The C_5-modified and hydrogenated resins commonly show excellent light stability; a major factor, especially for white road markings. The lightstable hydrogenated resins are not normally used because of their relatively high price. Some of the commercial C_5-modified resins also show remarkably good UV stability and are also used for white markings, depending on specific requirements.

C_9 resins show a gradually deteriorating light stability, though they are often used in combination with C_5 resins or in less sensitive areas. Because of their slight tendency to

yellow under the influence of light, indene-coumarone resins are not used at all. C_9 resins are primarily used in yellow road markings. For white road markings a higher pigmentation is suggested. A typical formulation is [5.15]:

- Long-oil linoleic-based alkyd resin (75 % solids)	11.2 %
- C_9 resin, low indene content, 105 °C R & B	5.0 %
- Chlorinated rubber	3.4 %
- Titanium dioxide	11.1 %
- Diatomaceous mica	6.2 %
- Calcium carbonate	36.3 %
- Micronized mica	8.7 %
- Toluene	11.7 %
- Bentonite gel (10 %)	5.0 %
- Soya bean lecithin	0.5 %
- Drier	0.6 %
- Anti-skinning agent	0.3 %

5.3.2.5 Temporary Rust Protection

For steel construction parts and especially in the automotive industry for underfloor and cavity protection as well as for some other applications, temporary rust protection is highly important for technical and commercial reasons.

Materials commonly used are normally composed of:

- Waxes (paraffin, microparaffin, oxidized paraffin, chloroparaffin, etc.)
- Hydrocarbon resins
- Anticorrosion agents (inhibitors)
- Solvents (Mineral oils, mineral spirits with low aromatic content)

Application is either by dipping or more often by spraying. In general the required resin profile is as follows:

- Solubility in mineral oils/solvent system
- Compatibility with waxes, paraffins, and chloroparaffins
- Resistance to aging
- High chemical resistance
- Light color
- Low odor

Resins, fulfilling these conditions are mainly:

- C_9 resins with high methyl substitution
- Phenol-modified C_9 resins
- C_5 resins
- Dicyclopentadiene resins
- C_4- or C_5-modified C_9 resins

Straight indene-coumarone resins are not suitable because of their poor solubility in mineral oils and lack of compatibility with waxes. The same is true for unmodified petroleum resins with a high indene content. Selection of a suitable resin depends in the

first place on the compatibility with the mineral oils and waxes used, and on the chemistry of the resin. This means that there is a very wide range of possibilities.

In spray application of the rust protection material, the lowest possible odor level of the resin component is required. A sufficiently long steam-stripping time in the final manufacturing step and selecting isothermal polymerization yields resins with a rather narrow molecular mass distribution, thus avoiding a higher percentage of odor-intensive low molecular mass components in the resin.

Major reasons for the use of hydrocarbon resins in temporary rust protection systems are their higher chemical resistance (salt water and condenser water), high film stability (hardness), high abrasion resistance, high heat stability, and ease of application. High filler loading is also possible [5.15].

A formulation example is:

- C_9 resin (α-methylstyrene/ vinyltoluene-rich, 120 °C R & B)	49 %
- Chlorinated paraffin	2.5 %
- Surfactants	1.5 %
- Solvent naphtha 90/160	47 %

5.3.3 Concrete Cure Membrane Coatings

Construction concrete requires water for chemical hydration to attain its final strength and dimensional stability. If concrete is not protected, excessive water loss may occur, owing to the heat of hydration and the effect of external heat (depending on ambient temperature), resulting in poor concrete quality. Thus, fresh concrete surfaces are often protected from too rapid drying by application of a coating which acts as a moisture barrier.

For this purpose, hydrocarbon resins, dissolved in mineral spirit or formulated as emulsion, are used. Application is mainly by spraying. Emulsions are preferred to solutions because the presence of solvent may cause health hazards and flammability problems, and also for price reasons.

Solvent-based cure membranes are low-viscosity solutions of an appropriate resin in mineral spirit. They may be supplemented by a fugitive dye to help control the quality of coverage, or (mainly for outdoor applications) by white pigment to reflect sunlight and to avoid overheating.

Emulsion formulations are mostly based on concentrated resin solutions dispersed in water with nonionic surfactants. Emulsions may cause problems with storage stability, especially at lower temperatures. For this reason, solvent-based membranes are still more usual than emulsions.

The concrete industry demands very low-priced products, based on cheap petroleum waxes, ester gums, and rosin, but these formulations have generally proved technically unsuitable. Hydrocarbon resins, because of their neutrality, high water repellency, and resistance to acids and alkalis are more suitable.

The most widely used resins are the unsaturated dicyclopentadiene resins, because of their oxydative self-degradation after curing is over. Within weeks they are easily brushed off. Other resins, insensitive to oxidative attack, such as C_5 or straight C_9 resins may also be

used. These resins will remain on the cured concrete, and may act as primers for further painting or additional coating.

5.3.4 Wood protection

Wood is very sensitive to humidity and biological attack and must be protected, especially when exposed outdoors. Hydrocarbon resins are widely used for this application, because of their water-repellent and fixing properties, i. e., fixing insecticides and fungicides in the wood, thus preventing "blooming" of the timber preservatives.

Two types of treatment are usual: impregnation and surface treatment.

5.3.4.1 Impregnation

Of major technical importance is the protection by impregnation with oils, resin solutions, or salt solutions, which penetrate deep into the structure of the wood (Figs. 5.11 and 5.12).

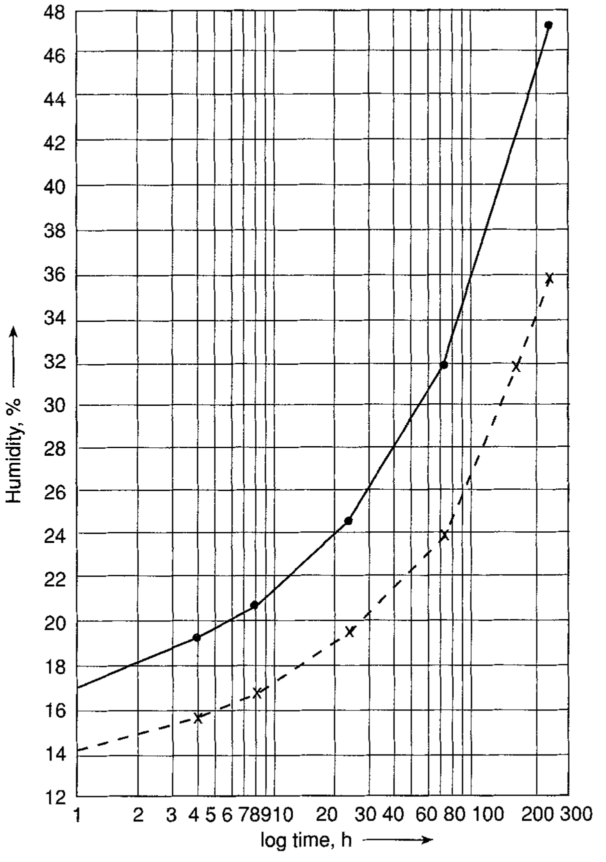


Figure 5.11 Water absorption of impregnated wood after immersion

Average of five samples. Dots = zero test; crosses = C_4-modified C_9 resin (7.5 %)

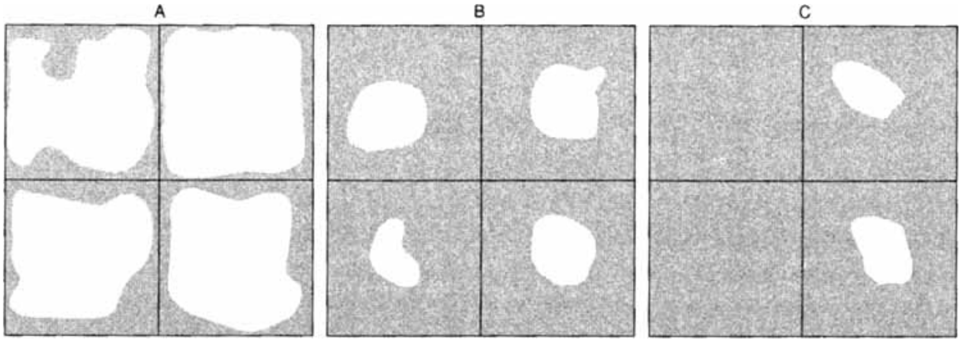


Figure 5.12 Penetration depth of resin solutions

A) Insufficient impregnation depth
B) Good impregnation (C_9 resin, 7.5 %)
C) Very good impregnation (C_4 modified C_9 resin, 7.5 %)

The earliest type of technical wood protection was impregnation by specially selected tar oils. A most effective method for the protection of railway sleepers, telegraph poles, etc., is timber treatment by pressure/vacuum impregnation (for instance the Double Ruping process) [5.16]. The impregnation of timber with a resin solution has many similarities to vacuum/pressure impregnation with oils (creosote oil, impregnation oil), still in use today. A process used in many countries is the so-called double-vacuum or vac-vac process (vac-vac is the protected trade name of Hickson's Timber Products, United Kingdom). In this process, excess pressure is avoided, resulting in simplification of the process. The double-vacuum process for the impregnation of timber with resin solutions is in use in the United Kingdom, Scandinavia, France, Spain, Portugal, The Netherlands, Australia, New Zealand, and the Middle East, among other countries.

Impregnation by the double-vacuum process involves a solution of an appropriate resin in an organic solvent, preferably mineral spirit. Additives are normally active substances (insecticides, fungicides) and occasionally small quantities of waxes.

From the wide range of mineral-spirit-soluble hydrocarbon resins, two types have proved themselves particularly useful:

- C_9 hydrocarbon resins with a higher percentage of α-methylstyrene/vinyltoluene
- the same resin, but aliphatic modified (C_4- and C_5-modified)

The first of these resin types should be custom manufactured, with very good solubility in mineral spirit. C_4- and C_5-modified aromatic hydrocarbon resins are particularly suitable.

Informative research work on wood (pine sapwood) impregnation by resin solutions has been carried out by the Wilhelm Klauditz Institute, Braunschweig (Fraunhofer-Institut für Holzforschung).

This application of resins requires good solubility in mineral spirit not only under normal conditions, but also at freezing temperatures. It has also be taken into account that, depending on the residence time of the impregnation solution in the tank, a slow oxidation may take place. This oxidation process, even though the extent of the oxidation in relation to the total mass of the volume of the impregnation solution is negligible, may cause

precipitation of microscopic resin particles, so that the fine pores in the microstructure of the timber may become clogged, and the impregnation effect is reduced.

The following formulation is given as an example for double-vacuum impregnation:

- C_9 hydrocarbon resin (softening point 100 °C R & B)	5.0–10.0 %
- Control pigment (e. g., non-light-fast dyes)	0.1–0.3 %
- Fungicidal agent	0.5–1.0 %
- Insecticidal agent	0.2–0.5 %
- Solvent	to 100 %

5.3.4.2 Surface Treatment

The best known means of wood protection is surface treatment with a covering paint, a clear lacquer, or an open-pored permeable wood stain.

Aromatic and other hydrocarbon resins are used in the formulation of low-odor, quick-drying primers, containing active ingredients for the protection of native and tropical timber against blue disease, mould, and other damage. The primer provides a smooth uniform surface for adhesion of all subsequent finishing coats. Nevertheless, the resin content is not detrimental to respiration.

The addition of the highly hydrophobic, chemically neutral resin greatly reinforces water repellency, which substantially reduces warping, swelling, and splitting of the timber. The reduction of water absorption is particularly evident in the case of pine. Dimensional stability is improved, especially important for timber construction elements. To what extent absorption can be reduced depends, among other factors, on the amount of resin additive (generally 25–30 %) and on length of exposure.

Resins are particularly used for the manufacture of so-called glazing compositions which are achieving an ever-increasing market share. Wood preservation glazings which contain suitable active components protect timber from mould, fungus, blue disease, decay, and insect attack. Unlike varnishes, these paint coats are porous, allow breathing of the timber, and facilitate subsequent coating. When redecorating there is no need to remove the glazing primer.

The increasing tendency to use glazing compositions is particularly due to the visual effect which may be obtained. The graining is preserved and enhanced. Furthermore, it is possible to imitate the appearance of exotic woods on domestic timber. The premature fading of valuable wood can largely be prevented.

Glazing paints containing hydrocarbon resins are odorless when dried out, and are preferably used for paneling in rooms, for windows, doors, etc. The coatings do not blister and cannot flake. Because of the resin content, resistance to acids and alkalis can be obtained.

The addition of resin also distinctly improves the sealing and impregnating effect of formulations based on linseed oil. If necessary, small quantities of wax/paraffin may be added. Furthermore, resin additives prevent bleeding of timber preservatives based on high-boiling oils. For internal use and to obtain a high-gloss effect, the glaze coating may be post-treated with clear varnish based on drying oils or synthetic resins.

Some suggested formulations are:

- Wood preservation glazing (interior use)

– C_9 hydrocarbon resin, 100 °C R & B	25.0–30.0 %
– Additives (anti-settling agent, fillers, etc.)	0.2– 0.5 %
– Organic pigment	0.3– 0.8 %
– Fungicidal agent	0.5– 1.5 %
– Insecticidal agent	0.2– 0.5 %
– Solvent	to 100 %

- Alkyd resin/hydrocarbon resin-based wood perservation glazing

– C_9 hydrocarbon resin, 100 °C R & B	5.0– 8.0 %
– Long-oil alkyd (60 % in white spirit)	12.0–15.0 %
– Organic pigment (depending on depth of color and glazing effect)	0.2– 2.0 %
– Fungicidal agent	0.5– 1.5 %
– Insecticidal agent	0.2– 0.5 %
– Drier (depending on alkyd resin quantity)	0.1– 0.3 %
– Solvent	to 100 %

95

5.3.5 Low-Solvent and Solvent-Free Varnishes and Coating Based on Epoxy and Other Binder Systems

Formulations based on epoxy resins, polyurethanes and various other binding systems often contain modifiers and extenders:

- to reduce viscosity
- to increase flexibility
- to improve chemical resistance
- to lower cost

The formulations may be solvent-based, solvent-free, clear or pigmented. By addition of neutral liquid resins, hardening time is increased and can thus be adjusted to special requirements; also pot-life is increased and flexibility of the coating is improved.

Liquid aromatic hydrocarbon resins are available as neutral low molecular oligomers or as reactive phenol-modified liquid oligomers.

Neutral liquid resins may be based on indene-coumarone feedstreams, on C_9 or especially processed C_9 streams, or on selected aromatic monomers with viscosities ca. 500–30 000 mPa. s at 25 °C and colors ranging from light to relatively dark (2–12 Gardner, undiluted). Neutral liquid resin types used in epoxy systems act as plasticizers. The difference, between neutral liquid resins and standard commercial plasticizers is the fact that the liquid resin is a polymer, albeit with a relatively low molecular mass. Nevertheless, the somewhat bigger and more rigid molecular structure of the neutral liquid resin lends the epoxy resin system more "backbone" than is achieved

with standard monomer plasticizer. In general, this special liquid resin fulfills most customer requirements.

However, it also has disadvantages. Under certain conditions, in epoxy coating formulations comprising a neutral liquid resin as modifier and extender, the liquid resin may migrate, giving the coating an oily surface. Therefore the paint industry demands a liquid modifier resin which is more intimately linked into the epoxy resin system when used as an extender. To meet this demand, resin manufacturers have developed activated liquid resin types, phenol-modified hydrocarbon resins containing hydroxyl groups. These activated types, though used as modifiers, diluents, or extenders, are not to be mistaken for the so-called reactive thinners, which are chemically entirely different.

Some manufactures offer liquid resins with different OH contents, ranging from 1.7 to ca. 2.7 %, as shown in Table 5.5.

Table 5.5 Range of special liquid resins

Type		Viscosity mPa. s(25 °C)	Gardner color	OH content %
A	Liquid C_9 resin	800–1 000	11–15	0
B	Liquid C_9 resin, phenol-modified	1 000–1 600	11–14	1.7–2.0
C	Liquid C_9 resin, phenol-modified	1 200–1 500	14–16	2.5–2.7
D	Liquid C_9 resin, phenol-modified*	700– 800	3– 6	2.2–2.4
E	Liquid C_9 resin, phenol-modified*	300– 400	3– 6	1.7–2.1

(* Improved light stability)

The incoporation of a phenol-modified C_9 resin in the epoxy system is based on a chemical reaction. This is described in more detail in Section 5.3.5.1.

For applications such as coatings exposed to intense sunlight, unwanted yellowing may occur with normal indene-coumarone or to a less extent, with C_9 feedstream-base liquid resins. For those applications, the special aromatic monomer-based types represent a substantial improvement.

In some cases, low viscosity is the decisive factor, and an activated liquid resin with improved light stability has been supplemented by a lower viscosity type (type E in Table 5.5). The lower OH content still allows good interlinkage in the epoxy resin system.

Excess of the liquid modifier can leed to a bleeding effect. This can be easily counteracted by reducing the extender quantity. Bleeding can also be observed in the event of incompatibility. In this connection it can be stated that these liquid resin types all show excellent compatibility.

The use of OH-modified liquid resins in epoxy systems has an influence on pot-life; with increased OH content, pot-life is reduced. The effect on hardening time is shown in Figure 5.13.

In principle, activated types are preferred for combination with polyurethanes. It should be noted, however, that the different activity of each individual activated liquid resin type applied in polyurethane resin systems, only becomes available when an accelerator is added, i. e., lead octoate, dibutyl tin dilaurate, amine catalyst.

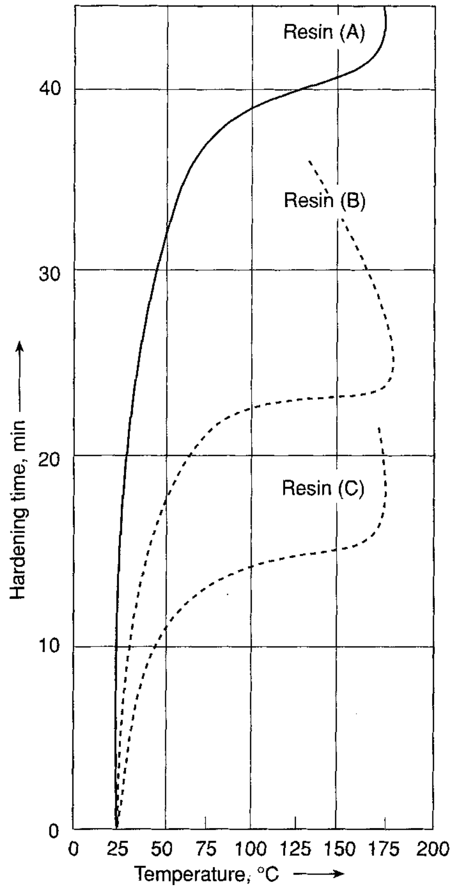


Figure 5.13 Hardening time as a function of temperature for epoxy/special liquid resin blends (60:40)

Resins are specified in Table 5.5

Apart from applications as modifiers in epoxy and/or polyurethane-based systems, special liquid resin types have also found use in formulating jointings and sealants based on polysulfides (see section 5.2).

In a similar area of application, activated slightly polar liquid resin types are used as modifiers for liquid functional polybutadienes, for instance "poly bd". By taking advantage of the special properties of activated liquid resin types, adaption of poly bd to various conditions and applications is possible. For more details see Sections 5.3.6.

Liquid resin binding agents are suitable in many varnish formulations as plasticizing components. In comparison with other products, the generally favourable price level makes this application attractive. Owing to the light color and the stability to light of some liquid resin types, they compete favourable with many plasticizers.

In the area of epoxy resin products, plasticizers play only a limited part, as many different plasticizing compounds are used, many of which are more expensive than the special liquid resin types. In particular, this involves low molecular mass acrylic compounds, and various copolymers, and also long-chain glycidyl ethers. The quality of performance depends on how such plasticizers are chemically built into the epoxy resin, if at all. The chemical interaction of activated special liquid resins in epoxy systems is described in Section 5.3.5.1.

Some suggested formulations are given below. In many of these, the liquid resins used improve the levelling and gloss of a film. It has been observed that combination with a liquid resin type in both solution and cured film can render two incompatible binding agents (or plasticizer and binding agent) compatible. In this respect, hydroxyl-containing activated liquid resin types and/or the corresponding liquid resins with increased light stability give better performance than the neutral liquid resins.

Generally speaking, the addition of special liquid resin types in the majority of formulations gives benefits other than merely acting as extenders.

In some cases, addition of more than 40 % (of total binding agent) is possible without disadvantage to the chemical or technical performance. In most formulations, the addition is in the range of 20 %, depending on pigmentation requirements.

Some general formulations are given below.

- Anticorrosion coating, black, high gloss:

– Epoxy resin	25.0 wt %
– Phenol-modified liquid C_9 resin	12.5 wt %
– Iron oxide	42.8 wt %
– Filler	7.6 wt %
– Hardener type 1	7.5 wt %
– Hardener type 2	4.6 wt %

Such flexible varnishes have good levelling properties. The glossy metallic film and good adhesion properties guarantee resistance to heat, UV, and industrial gases. Addition of small amounts of leafing aluminum powder or color pastes enables the optical properties to be adjusted. The addition of the activated liquid resin can be reduced or increased according to the flexibility requirements.

- Coating for steel parts and mineral surfaces:

– Epoxy resin	20.2 wt %
– Phenol-modified liquid C_9 resin	11.2 wt %
– Iron oxide	37.2 wt %
– Silicon carbide	12.4 wt %
– Butyl glycidyl ether (reactive thinner)	8.8 wt %
– Hardener type 1	6.2 wt %
– Hardener type 2	2.2 wt %
– Accelerator	1.8 wt %

The dark-grey coating is low gloss, very flexible (breaking point 360 °C), shows good levelling proporties, and good covering. The hardness is satisfactory or good for

most applications, but can be increased by a reduction in the amount of liquid resin. Silicon carbide increases resistance (stability), hardness, and covering power. The coating must not be ground, because this destroys the lamellar structure of the iron oxide. Stirring is satisfactory because it allows the silicon carbide to disperse easily.

- Coating for steel parts:

- Epoxy resin	26.4 wt %
- Zink phosphate	30.0 wt %
- Zink borate	14.6 wt %
- Filler	8.0 wt %
- Butyl glycidyl ether (reactive thinner)	3.0 wt %
- Phenol-modified liquid C_9 resin	5.0 wt %
- Yellow pigment	1.2 wt %
- Hardener	11.8 wt %

The coating is glossy, has good levelling properties, and is flexible. Covering power can be increased by adding more pigment. Zinc phosphate has proved itself to be an anticorrosive pigment.

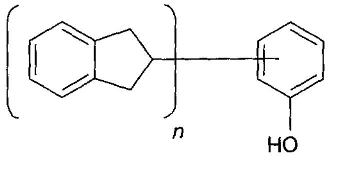
Zinc borate also has flame-retardant characteristics. Additives to improve surface hardness are not necessary. The coating maintains its flexibility, owing to the presence of the phenol-modified liquid C_9 resin, which also improves gloss.

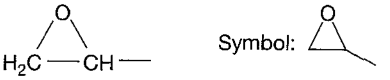
Special liquid resins are used as modifiers in combination with epoxy compounds and/or polyurethanes in structural engineering, civil engineering, water engineering, and steel girder construction. They can be formulated into thick and thin film systems. They are suitable for lining of vessels, floor coatings, joint sealing compounds, sound proofing, underseal protection, adhesives, insulating compounds for the electrical industry, concrete adhesives, and roof coatings, among other areas of application. The customer, however, must carry out an evaluation program to determine the suitability of a particular special liquid resin for a specific application.

5.3.5.1 Chemistry of Activated Special Liquid Resins in Epoxy Systems [5.17]

Because of the wide interest in activated special liquid resins (aSLR) as modifiers, diluents, and extenders in epoxy-based systems, a more detailed description of the chemistry involved is given here. The following reaction mechanism is proposed.

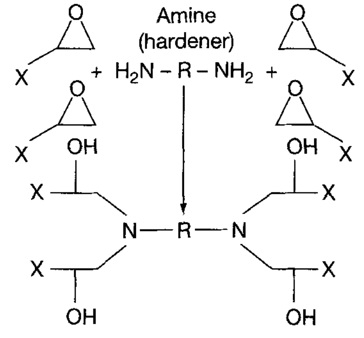
The indene-based aSLR-types are chemically a complex mixture of aromatic copolymer hydrocarbons. They can be considered as derivatives of indene. The basic chemical structure of an aSLR is as follows:



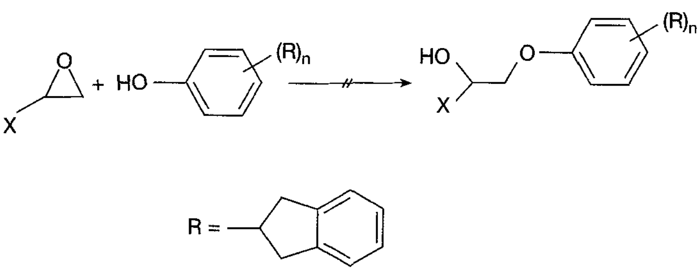


The resins differ from other aromatic hydrocarbon resins because of the presence of phenolic OH groups. Typical of all epoxy resins is the three-membered epoxy ring system consisting of an oxygen atom and two carbon atoms:

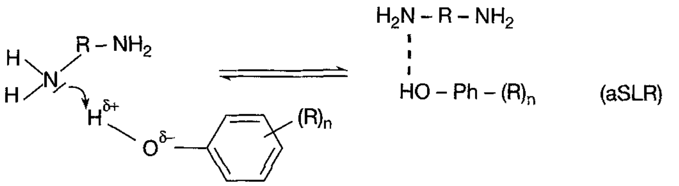
Depending on temperature and catalytic activation, this epoxy ring reacts with a multitude of compounds (nucleophilic reaction with the epoxy ring). For example, amino groups of aliphatic polyamines such as isophoronediamine or diethylenetriamine react (harden) with the epoxy ring of the epoxy resins with the formation of stable hydrocarbonyl-nitrogen compounds:



At room temperature, addition of the phenolic OH group to the epoxy ring does not occur. This reaction becomes significant only above 60 °C, in the presence of an accelerator, for instance, a tertiary amine:

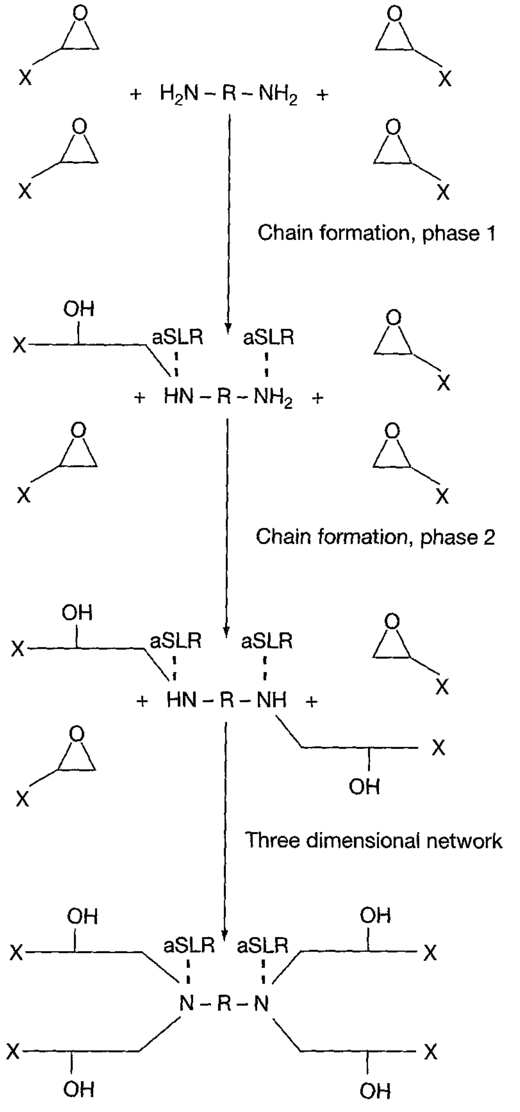


After mixing the phenolic hydrocarbon resin with the amine curing agents, a spontaneous increase of viscosity and heat evolution can be observed: the phenolic OH group is polar; the positively charged hydrogen atom interacts strongly with the free pair of electrons on the nitrogen atom of the amine:



Energy is released as the amine and the phenolic OH group associate. The binding energy is equivalent to ca. 10 % of that of a typical covalent bond.

Before the epoxy resin can react with such a stabilized primary amino group, the electrostatic bonding has to be broken by absorption of energy. Reaction of the epoxy resin is then possible with the free electron pair of the nitrogen atom. The secondary nitrogen atom thus formed (chain formation, phase 1) is then able to associate with the polar OH group of an aSLR molecule. In the hardener molecule there are now two chemically different reactive nitrogen atoms available as reaction centers, a secondary and a primary nitrogen atom. The velocity of reaction of both unassociated nitrogen atoms is not greatly



different, but association results in a considerable preference for further reaction at the primary nitrogen atom, and at the same time induces linear bonding of the resin and the hardener molecule (chain formation, phase 2).

It is only in the subsequent reaction process that the electrostatic bonding is broken again by absorption of energy, at the secondary nitrogen atom. The free N-H bonds then react completely with the epoxy resin to a three-dimensional network. The network is very regular, resulting in a high degree of hardening, i.e ., there is only a very low residual content of unreacted resin and hardener molecules.

After hardening, the phenolic substances are encapsuled in the three-dimensional network. The phenolic OH group does not react with the epoxy rings. In addition to encapsulation in the molecular network, a high percentage of the aSLR molecules are bound physically to the now tertiary nitrogen molecules by means of the electrostatic attraction described.

The use of activated special liquid resins in hardening epoxy resins with amines leads to:

- the formation of linear polymer chains at the beginning of the hardening process
- the formation of regular three-dimensional molecular networks toward the end of hardening
- high degree of hardening
- physical bonding to the hardened binder via the polar phenolic OH groups

All these effects contribute to the positive properties of epoxy formulations with activated special liquid resins.

5.3.6 Polyurethane Coatings

Polyurethane coatings, sealants, and various other applications may be modified by aromatic liquid hydrocarbon resins.

Polyurethane chemistry is based on the reaction of the isocyanate group (NCO) with hydrogen-reactive functional groups, for instance R-OH, R-NH_2, R-COOH, etc.

Isocyanates and polyisocyanates are commonly considered as hardener components. As there is a large number of polyisocyanates, the number of different resin components is almost unlimited.

Polyurethane resin (PUR) formulations for compact systems, for example, industrial floor coatings, sealants, molding compounds, paints, primers, are predominantly based on the hardener component diphenylmethanediisocyanate (MDI) in combination with polyether- and/or polyester polyols (resin component).

Special liquid resins have proved to be useful modifiers for polyurethane formulations. Neutral, unreactive special liquid resin (a low molecular mass polyindene resin) can be added to the isocyanate component in order to achieve a favourable ratio of resin and hardener component.

The unreacted liquid resin is miscible and compatible in all proportions with aromatic isocyanates, for instance with MDI, and also has good storage stability.

The activated special liquid resins are phenol-modified resins of variable OH content. The activated types have therefore to be added to the resin component. They show full compatibility with most commercial polyether and polyester polyols.

When using special liquid resins as modifiers in PUR formulations the following effects can be achieved:

- Regulation of viscosity
- Wetting of fillers
- Elastification (in many cases)
- Increase in hydrophobic character

The hydrophobic effect of the special liquid resins shows during the hardening in a smooth, bubble-free surface, even at longer hardening times, as well as in the hardened compound showing lower water absorption on immersion.

The addition of special liquid resins to short-chain aliphatic polyol blends also improves their compatibility with aromatic polyisocyanates at room temperature. Depending on the individual formulation and end properties, addition of 10–30 % of the liquid resin to the unfilled or filled resin components is suggested.

Apart from activated special liquid resins, other modified resins can also be used for the modification of polyurethanes, for example, phenol-modified, OH-groups containing indene-coumarone resins with softening point 45 and 90 °C R & B. They can replace 10–30 % of the polyol component (for example, Desmophen 550 U and/or 1 150) in PUR systems.

The highest viscosity is obtained with the higher melting resin type, but even with 30 % addition (on the polyol) the resulting viscosity is still within the viscosity range of commercial polyols. Adding 30 % phenol-modified indene-coumarone resin does not reduce the shore hardness of a PUR molding compound. A hydrophobic effect can also be observed. Thermal stability is the same as that of a pure PUR system.

• A suggested formulation for a **hard compound** (parts per weight) is:

- Branched polyether 1	200
- Branched polyether 2	300
- Dehydrated castor oil	250
- Special liquid resin, activated	150
- Silica, high-dispersed	2
- Deaerating agent	1
- Zeolite paste	97
Resin component A	1 000
Hardener component B	isocyanate
(mixing ratio A : B = 100 : 50)	

• A tentative formulation for a **tough elastic compound** (part by weight) is:

- Branched polyether	120
- Dehydrated castor oil	467
- Special liquid resin, activated	330
- Silica, high-dispersed	2

- Deaerating agent	1
- Zeolite paste	80
Resin component A	1 000
Hardener component B	isocyanate
(mixing ratio A : B = 100 : 35)	

Tests of modified polyurethane molding resin compounds have shown that, with selected polyols, there is a clearly improved compatibility with the isocyanates. Furthermore, it has been found that in the water immersion test, water absorption decreases with increasing quantity of activated liquid resin added to the formulation, i. e., the hydrophobic properties of the compound are improved.

At this point it should be mentioned that special liquid resins are also very useful in the modification of PUR formulations on the basis of the so-called poly bd resin, a liquid polybutadiene with terminal hydroxyl groups [5.18].

Because of its primary hydroxyl groups and its high content of unsaturated C=C bonds, the poly bd resin shows high reactivity, especially in polyaddition with polyfunctional isocyanates, etc. PUR formulations manufactured on the basis of poly bd resin exhibit excellent hydrolysis stability, high flexibility, and very good dielectric properties. Poly bd PUR formulations find use in sealants, elastic coatings and binders in sports facilities, protective coatings against acids, etc. Owing to the good compatibility of special liquid hydrocarbon resins with poly bd, there is the opportunity for modification and adaptation for specific applications. Many years of experience have shown that slightly polar special liquid resins are particularly well suited for modification purposes, for instance the various types of activated liquid resins with phenolic OH groups, which have proved their merits in combination with epoxy compounds and polyurethanes in high-duty coatings, sealants, marine paints, and many other areas.

Depending on the formulation and application, the quantity of special liquid resin added may vary between 10 and 50 parts by weight to 100 parts of poly bd.

The addition of special liquid resins offers the following advantages:

- Lowering the viscosity of poly bd resins
- Easier processing
- Improved filler and pigment wetting
- Improved compatibility of the poly bd resin and polyols
- Improved adhesion
- Increased chemical resistance
- Price reduction

• A suggested formulation for a **low-modulus, pourable, self-levelling system** (parts by weight) is:

A - Liquid polybutadiene with terminal OH groups	100
- 2-Ethyl-1,3-hexanediol	2
- Plasticizer	40
- Special liquid resin, activated	10
- Filler	75
- Carbon black	2

	- Antioxidant	0.5
	- Dessicant	3
	- Catalyst	0.015
B	- Isocyanate (NCO/OH ratio = 1.05)	16.6

Components A are blended by stirring and degassed for 30 min. Mixing ratio A : B = 100 : 7.1.

• A suggested formulation for a **high modulus, pourable self-levelling** system (parts by weight) is:

A	- Liquid polybutadiene with terminal OH groups	100
	- 2-Ethyl-1,3-hexanediol	20
	- Special liquid resin, activated	20
	- Defoamer	0.2
	- Dessicant	3
	- Antioxidant	0.5
	- Filler	75
	- Carbon black	1
	- Catalyst	0.01
B	- Isocyanate (NCO/OH ratio = 1.05)	54.5

Components A are blended by stirring and degassed for 30 min. Mixing ratio A : B = 100 : 24.75.

In both examples [5.18], the sheets are cured for 25 h at 23 °C in open moulds and post-cured for 24 h at 80 °C.

5.3.7 Bituminous Materials

Asphalt and coal-tar pitch, used in road and pavements, roof, pipe, automotive undercoatings and various water barrier coatings may be upgraded and modified by hydrocarbon resins. Such resins are:

- C_5 aliphatic
- C_9 aromatic
- C_4/C_9 and C_5/C_9 mixed resins types
- Dicyclopentadiene resins
- Indene-coumarone resins
- Tall oil rosin

Coal-tar-based coatings applied to prevent general deterioration of interior or exterior walls use some indene-coumarone and C_9 hydrocarbon resins. Moisture resistance, alkali and acid resistance, toughness, and surface characteristics, such as gloss and smoothness, are improved.

5.3.8 Fruit Preservation

A further specialized application of hydrocarbon resins, used as coatings is in fruit preservation. For many decades indene-coumarone resins and similar aromatic hydrocarbon resins have been used in the preservation of citrus fruit oranges, grapefruit, lemons, limes, tangarines, etc. i. e., for preservation of thick-skinned fruit types.

As resins in this area of application are used as food additives, they have to conform to certain regulations. According to FDA regulations, the resins have to be original coal-tar-based indene-coumarone resins with a minimum softening point 126 °C R & B, and the quantity remaining on the fruit after treatment must not exceed 200 ppm on a fresh-weight basis. Other regulations limit the maximum quantity to 140 mg/kg fruit, either alone or in a mixture.

Usually the resins are used in combination with natural waxes, which requires a resin with sufficient wax compatibility. Sometimes small quantities of active protective additives (fungicides) are found in these formulations.

There are a number of reasons why resin-containing formulations are used in citrus fruit conservation:

- the protective coating prevents the quick drying-out of the fruit, i. e., evaporation of water through the peel
- at the same time, the coating protects the fruit from microbes (rot bacteria, etc.) which may enter the fruit through the fine pores of the peel
- the coated fruit surface gives excellent gloss on mechanical polishing

The protective coating is commonly applied as a resin or resin/wax solution by spraying, brushing, or dipping in an impregnation machine, with a subsequent drying (evaporation) step. The evaporated solvent is recovered and recycled. It is also possible to apply the formulation as a dispersion. There is a trend to switch from aromatic solvents to mineral spirits, blends of hexane and heptane, etc., which means that the solubility of the resins used is of some importance.

5.4 Printing Inks

Hydrocarbon resins are used in printing inks because of their compatibility with many ink components, e. g., alkyds, oils, and ink solvents, as well as their good resistance to water and alkali. Pigment wetting and solvent release are also important factors. Appropriate selection of feedstreams, careful control of manufacturing processes, and quality assurance ensure the supply of useful resins to the ink industry.

5.4.1 Printing Processes

In the formulation of printing inks the special requirements of different printing methods have to be taken into consideration. The major printing systems are:

Table 5.6 Printing systems

Process	Type
Letterpress	Sheet-fed
Lithography/offset	Sheet-fed
	Web-fed
Gravure	Rotary
Screen	Sheet-fed
Flexography	Rotary
Xerography	Sheet-fed

- **Letterpress**

is the oldest of these printing processes. The ink is applied to the raised part of the printing plate. The system consists of a flat image plate, an ink roller to apply the ink, and a further plate which presses the paper sheet onto the printing plate, thus transferring the ink to the substrate. This method has a low printing speed. Higher printing speeds are made possible by a rotary method where both parts of the device are cylindrical. Both sheet and web type may be used. Letterpress printing is used for newspapers and books, magazines, etc.

- **Flexography**

is a special type of letterpress using a rubber printing plate. This method is used for printing on plastic film, metallic foil, and paperboard.

- **Offset printing**

is a planographic printing system in which the printing and the nonprinting areas are on the same level.

By photochemical and photomechanical processes the image area is made hydrophobic (oil receptive) while the non-printing area is hydrophilic (water receptive). The plate is first covered with a layer of water which is repelled by the printing areas. Immediately afterward, the fatty ink is fed from a separate series of rollers to the cylindrical printing plate, where it adheres only to the hydrophopic printing areas. From the printing plate the ink is transferred to an intermediate rubber-covered roller (offset blanket) and from there to the substrate. Offset printing is used for newspapers, books, and magazines.

- **Gravure printing**

is a method in which the ink is applied to a chemically etched or mechanically engraved plated cylinder, i. e., the ink is below the printing surface, in the recessed parts of the plate. After the excess ink is removed by a "doctor blade", the ink is transferred from the recessed parts to the paper. This printing method is of high quality. It is used for printing high-quality magazines, letterheads, visiting cards, etc.

- **Screen printing**

is similar to textile printing. A viscous paint-like ink is pressed through a fine-meshed screen where the nonimage areas are blocked. Apart from the graphic sector, screen printing is used in decorating glass and ceramics, electrical circuit boards, traffic signs, etc.

- **Xerography**

is an electrostatical process, employing a special powder ink. This ink, bearing a negative charge, is blown onto a specially treated aluminum plate, where the positive image parts attract the ink particles. From there the ink is transferred to the paper and fixed by heat.

5.4.2 Ink Formulations

Table 5.7 shows the major components of letterpress and offset ink formulations.

Table 5.7 Components of letterpress and offset inks

Component	Function
Vehicle:	
Hard resin	Gloss, film hardness, and setting
Drying oils/alkyds	On-press properties, oxidative drying
Other components:	
Pigments	Color
Driers	Accelleration of oxidative drying
Waxes and other additives	Special ink properties

The ink vehicle contributes the properties that enable an ink to perform on the press and on the substrate. The major requirements from the vehicle are: It is a carrier for the pigment, and must allow the optimum performance from the pigment. It is balanced to meet the chemical and physical demands of the printing press, both during printing and on the substrate immediately after printing. It must be formulated to give the properties demanded from the final printed product.

Before discussing ink resins, some of the above properties should be described in greater detail.

- **Pigment wetting**
  In order to achieve the optimum strength, optical brightness and cleanliness of color, the ink must have good pigment wetting properties. A high degree of polarity in a rosin, or oil-based resin, as measured by acid number, gives good wetting, but the restrictions of the lithographic process places a limitation on this. Some neutral resins are also excellent, and can be used in combination with the above.

- **Rheology/Flow behaviour**
  The ability of an ink to be fed evenly onto the press, and then to transfer over the often complex series of rollers at very high speed, onto the paper is dependent on the solution stability, rheology, and tack of the varnish.

- **Drying of the ink**
  This is a two-stage process, initial setting by loss of solvent from the ink film, followed by a slower evaporation of residual solvent traces or an oxidation stage, depending on the ink type. With heatset systems these two stages occur simultaneously, for sheet-fed presses much slower, whereas for coldset web systems there is no oxidative stage

- **Mineral oil tolerance (MOT)**
  This is a measure of the compatibility of the hard resins with the mineral oil, or the degree of solubility of the system. The MOT is in direct proportion to the resistance of the system to separate under high rates of shear, and can be a measure of the ability of the ink to transfer on the press.

Many of the above requirements of the ink act in oppostion to each other. Extremely fast setting can cause press transfer problems; high gloss can lead to set-off in the stack, or on rewind.

5.4.3 Ink Resins

In modern ink varnishes a wide variety of synthetic resins can be used:

- alkyd resins
- rosin-based resins
- hydrocarbon resins
- acrylic resins
- nitrocellulose
- styrene resins

For lithographic and letterpress inks only the first three resins are used, and they have to be selected for their solubility in the high-boiling solvents needed for these processes. These solvents are mainly aliphatic, with a varying degree of aromaticity up to 20 %. Boiling ranges are in excess of 250 °C, and their solvent power is relatively low.

Resins with lower softening points are very rarely used as they are very low in viscosity, with a high tack, and exhibit too high affinity for solvents. Higher melting resins used in ink formulations are listed in Table 5.8.

Table 5.8 Resins in ink applications

Resin type	Softening point °C R & B	Acid number
Alkyd resins	liquid	5–12
Modified rosin resins	135–180	20–30
C_9 aromatic resins	120–170	1
Dicyclopentadiene resins	120–170	1
Indene-coumarone resins	120–170	1
Modified hydrocarbon resins	130–170	10–20

These resins are usually used in combinations to optimize the properties from each.

For rosin resins, the lower softening point versions have better pigment wetting, low viscosity, and poor solvent release. As the softening point is increased, these properties reverse.

The hydrocarbon resins, in general, are similar to the lower softening point rosin resins, in that they are low viscosity, and poor solvent release. Pigment wetting is inferior, but the tack is lower at a given viscosity. Unmodified hydrocarbon resins are neutral, and are considered hydrophobic when used in lithography. Alkyd resins are liquid and supplied at 20–1 000 poises. Their use in varnishes aids press performance, and also helps to solubilize the hard resins. In sheet-fed inks they oxidize to give a hard glossy film.

5.4.4 Resins for Printing Processes

- **Letterpress inks**

  In general this process is disappearing for conventional printing, although there are specific applications for which the process is ideal. These applications use very specific resin systems, and are beyond the scope of this book. The sheet-fed inks for this process now use sheet-fed lithographic inks, rather than special formulations. Newspaper inks, for printing by this process are extremely simple and often contain only carbon black and mineral oil, but may also contain hydrocarbon resins.

- **Lithographic inks**

  Inks for this process can, technically, be devided into three categories:

  - Sheet-fed, offset
  - Web offset, heatset
  - Web offset, coldset

  As the name implies, the first type prints the substrate in sheets. At the delivery end of the press the sheets are collected in stacks. This requires the ink to set by absorption of the mineral oil into the paper with sufficient speed to prevent the sheets from sticking to, or the ink setting off onto the next sheet. This necessitates good solvent release by the resin, but not too fast as to cause separation on the rollers of the press. These inks then dry hard by oxidation over about 4 h while in the stack. A typical formulation for a quickset ink is shown in Table 5.9.

Table 5.9 Composition of an offset ink (quickset)

Component	Quantity, %	Value, %
Pigment	22	71
Hard resin	28	15
Alkyd resin	10	5
Mineral oil	35	5
Driers	2	1
Wax/Additives	3	2

The hard resin part is a mixture of various grades of rosin-based resins. Non-functional hydrocarbon resins are rarely used in these inks.

- **Web offset heatset**

presses are fed by a reel of paper, which after printing passes through a drying oven at ca. 100–130 °C. From the oven the inks are hard dry, and while some applications result in the web being re-wound, often the web is cut and folded, in line, to result in a section of the finished magazin. Once again the ink formula has to balance the needs of good transfer through the press against high-speed drying. In comparison to the above formula, the pigment is slightly reduced, as is the alkyd component. The driers are omitted, and the mineral oil is marginally more volatile. In these inks it is very common for a proportion of the hard resin to be a hydrocarbon resin.

- The **web offset coldset**

process is most commonly used in the newspaper industry. Therefore printing is done on a very absorbent substrate, and does not require heat to dry.

Again the paper is immediately cut and folded to produce the complete newspaper, in line. This requires very fast absorption of the mineral oil into the stock, but the newsprint is very receptive.

The ink formula evolves further to give lower pigment, reduced alkyd, increased mineral oil, and reduced hard resin. Again no driers are used and very little additive. Econom~~om~~y is important in these inks, and this, together with the need for good solubility at low resin content, results in the extensive use of hydrocarbon resins.

As indicated, hydrocarbon resins do have their applications in lithographic printing inks. Their benefits can be summarized as:

- Low viscosity
- Excellent solubility
- Fair pigment wetting
- Low tack compared to equivalent rosin resin
- Good economics compared to equivalent rosin resin
- Used to adjust ink/water balance

A range of formulations for ink vehicles (parts by weight) is available. Some examples are given below [5.19].

- News black vehicle (rotary letterpress)

A	C_9 petroleum resin, 100 °C R & B	7
	Spindle oil	3
B	Spindle oil	90

- Web offset news ink vehicle:

A	Phenol-modified rosin ester	21
	C_9/DCPD resin, 160 °C R & B	21
	Alkyd resin	8
	Ink oil 280–310 °C	20
B	Ink oil 280–310 °C	30

- Heat-set offset vehicle:

A	Phenol-modified rosin ester	20
	Modified DCPD resin with carboxyl groups, 150 °C R & B	26
	Alkyd resins	8
	Ink oil 240–270 °C	26
B	Ink oil 240–270 °C	20

- Sheet-fed offset vehicle:

A	phenol-modified rosin ester	40
	C_9/DCPD resin, 150 °C R & B	10
	Alkyd resin	10
	Ink oil 280–310 °C	20
B	Ink oil 280–310 °C	20

Components **A** are high-speed dissolved; component **B** is then added and the two components are mixed.

- **Gravure inks**

These inks are mainly based on phenolic-modified rosin, resinates, and functional hydrocarbon resins. The main solvents are toluene and white spirit (60–130 °C).

Nonfunctional resins, for example C_9 resins with a high indene content and softening points 140–150 °C R & B as well as indene-coumarone resins with softening points ca. 160–170 °C R & B, have found place in some special illustration rotogravure inks. These resins are normally used in combination with resinates.

In practice, the normally high-viscosity pigment dispersions (pastes) found in vehicles made from typical ink resins are adjusted to printing consistency by the addition of an extender varnish, and possibly by some extra toluene.

Partial replacement of ca. 20 % resinates in the extender varnish is possible with a 150–170 °C R & B indene-coumarone resin. For etched printing plates with higher color volumes, adding too much 150–170 °C R & B IC resin can lead to solvent retention and possibly blocking.

When used as first color in four-color printing, i. e., when the paper still has its full absorption capacity, practically no problems are to be expected.

In publication gravure and packaging printing, inks based on modified rosin esters are increasingly replaced by acrylic-based systems.

- ***Flexographic inks***

These ink systems utilize only small amounts of rosin esters. The trend is to polyamide-based, alcohol-soluble systems and water-based acrylic emulsions. In special packaging inks, the expensive ketone resins may be partially replaced by phenol-modified indene-coumarone resins with softening point ca. 120 °C R & B. When used with the usual solvents, such as ethanol and low boiling esters, modified IC resin 120 °C R & B offers adequate solubility and at the same time facilitates quick solvent release.

- **Screen printing inks**

Screen inks are of paint-like, paste consistency. They are based on a wide variety of binders, depending on the substrate. Examples are solvent-based inks, using rosin esters and their salts (resinates), together with alkyd resins. Hydrocarbon resins are rarely used. Water-based inks are formulated with acrylic emulsions and do not need additional resins.

- **Xerographic inks**

They are powders consisting of pigments and finely powdered resins. Electrostatic properties and softening point range are important factors in the choice of an appropriate binder (normally styrene-butylacrylate, styrene-butylmethacrylate, together with vinyltoluene-butadiene). A classical developer is composed mainly of iron particles (98 %) and a toner (2 %).

- **Water-based inks**

These systems have aroused considerable interest because of increasing regulation of solvent emissions. Water-based ink systems are formulated on the basis of acrylic polymer emulsions. Ink resins of this type do not need additional resins.

5.5 Rubber Tires and Mechanical Rubber Goods

Rubber stocks are compounded with a multitude of different additives, such as processing aids, plasticizers, reinforcing agents, tackifiers, pigments, antioxidants, and curing agents.

Resins are widely used in this application. They are generally referred to as processing aids, but in fact, their function in rubber mixtures is multiple. They work as processing aids as well as for achieving special properties of the finished goods.

Typical resins for these applications are:

- Indene-coumarone resins
- C_9 aromatic resins
- C_5 aliphatic resins
- Mixed aromatic/aliphatic resins
- Dicyclopentadiene resins
- p-Alkylated phenol resins
- Unmodified rosin

Alkyl phenolic resins represent the largest volume, followed by hydrocarbon resins. Low-priced rosin and derivatives are used only at a low level.

Hydrocarbon resins promote processing by lowering viscosity, and improve building tack of the unvulcanized mixture. Properties of vulcanized mixtures such as elongation, tensile strength, and flex resistance may be improved.

The first resins to be widely used in rubber compounding for tires and mechanical goods were the aromatic indene-coumarone resins. With the rise of the petroleum industry, aliphatic hydrocarbon resins became available in large quantities, mainly in the United States, where steam-cracker raw material generates mainly aliphatic resin feedstock. Because of this historical development, and lower availability of the classical indene-coumarone resins in the United States, there was an increased tendency to use aliphatic petroleum resins in the rubber industry, mainly in tire production. However, there is no real technical reason for the use of one or the other type of resin. The main influences on choice are availability, consistency, and price.

5.5.1 Tires

The main elastomers used in tire production are natural rubber, SBR, and polybutadiene, often used as blends. Despite extensive research, rubber compounding for tires is still largely based on empirical knowledge, and changes to established processes tend to be very expensive.

5.5.1.1 Tire construction

The first step in tire construction is assembly of the rubber-coated fabric. Typically, polyester tire cord is used for the carcass, with steel wire belting for stiffness. Before fashioning into plies, the tire cord must be prepared to guarantee adhesion to the rubber. Then follows calendering. The fabric is contacted with the rubber stock by passing between rollers under controlled conditions of temperature, tension, speed, etc. After calendering,

the fabric is fed to the building drum. First the inner liner is applied, then plies, beads, and chamfers are added, followed by belts, tread, and sidewalls. During this building and forming step, the different uncured elements must hold together perfectly. The necessary "green tack" is furnished by tackifying resins. Finally, the "green" tires are vulcanized under pressure and heat.

The main use of resins in the tire industry is to improve compounding properties, i. e. promotion of green tack and regulation of the viscosity of raw mixtures. Incorporation of resins may also have positive effects on vulcanization behavior, and on the characteristics of the finished product.

Some indication of the influence of resins is given in the following comparison of different resin types in a test formulation for tire mixtures [5.20].

- Test formulation (parts by weight):

- SBR	100
- ZnO	5
- Stearic acid	2
- Carbon black	60
- Plasticizer	5
Antiaging agent	1
- Sulfur	2
- Accelerator	1.5
- Resin	0 and 5

Formulation with A) no resin
B) aliphatic C_5 resin
C) indene-coumarone resin
D) aromatic C_9 resin
Resin softening point, ca. 100 °C R & B

5.5.1.2 Properties of Unvulcanized Mixtures

Mooney viscosity, green tack and tensile strength have been tested.

- **Mooney viscosity**

Lowering of viscosity to improve processing properties of rubber stocks may be achieved by addition of oil, plasticizer, and/or resins. While the presence of oil or plasticizer has a rather negative influence on the properties of the vulcanized mixture, use of resins may balance this handicap, or even improve the mechanical properties of the vulcanizates.

The Mooney viscosity (Fig. 5.14) is lowered by addition of a hydrocarbon resin, and/or a plasticizer, compared to a standard mixture containing none of both.

- **Green tack**

(Fig. 5.15) is improved by resin addition, the highest value being obtained with the aromatic C_9 resin.

- **Increase of tensile strength**

is more or less independent of resin type (Fig. 5.16).

5.5.1.3 Influence of Vulcanization

Measurement of the torsional moment (torque) and scorch time gives the following results: The difference between the maximum and minimum torque (C_M-C_m) which is a

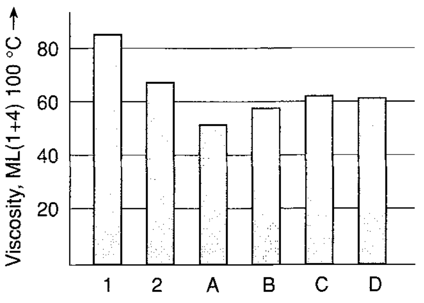


Figure 5.14 Mooney viscosity

1 Test formulation without resin or plasticizer
2 Test formulation containing only resin (aromatic C_9 resin, 100 °C R & B, 10 parts)

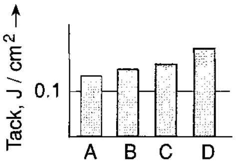


Figure 5.15 Green tack

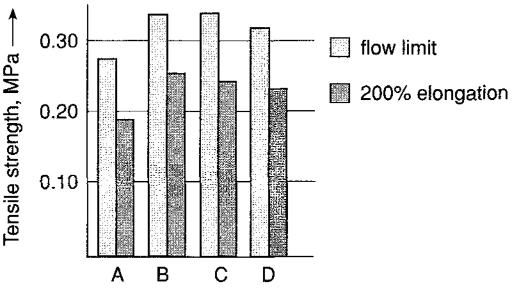


Figure 5.16 Tensile strength

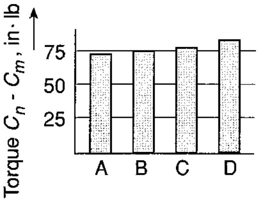


Figure 5.17 Difference between maximum and minimum torque

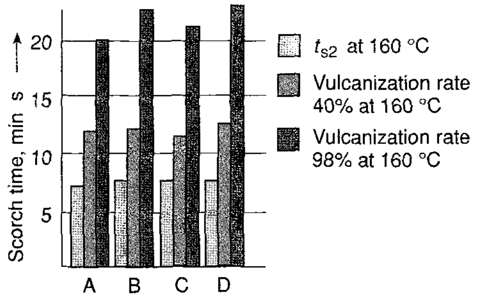


Figure 5.18 Scorch time

measure of reticulation density, is increased. The highest value is obtained with C_9 resins (Fig. 5.17).

Scorche time is essentially unaffected by the presence of resin (Fig. 5.18).

5.5.1.4 Mechanical Properties of Vulcanizates

- Elastic modulus, both at 100 % and 300 %, hardness, remanence after compression, breaking elongation, tensile strength at break, and tear propagation strength are maintained or somewhat improved compared with the control vulcanizate (Fig. 5.19). The change of modulus at 100 % and 300 % is negligible.
- Hardness is almost the same as that of the control (Fig. 5.20).
- Remanence after compression is almost equal to that of the control, with the exception of the aliphatic resin, which has an appreciably lower value (Fig. 5.21).
- Tensile strength at break as well as tear propagation strength are comparable to control for all resins, even after aging (Fig. 5.22 and 5.23).
- Breaking elongation improves slightly for the aromatic resin types, but is somewhat lowered by the presence of the aliphatic resin. After aging, this property is slightly improved for all resins, with a slight advantage for the C_5 resin (Fig. 5.25).

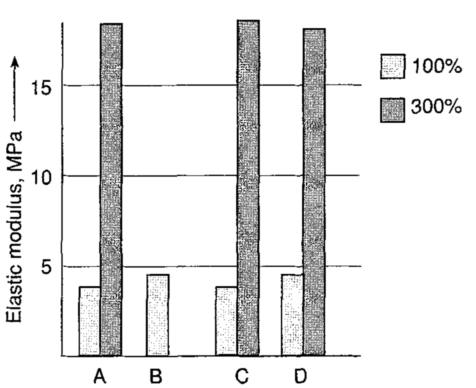


Figure 5.19 Elastic modulus

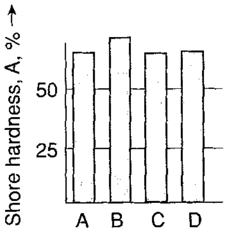


Figure 5.20 Shore hardness

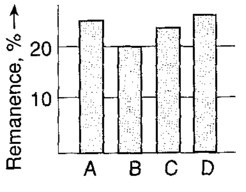


Figure 5.21 Remanence after compression

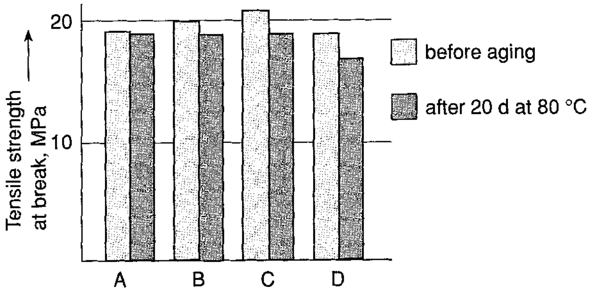


Figure 5.22 Tensile strength at break

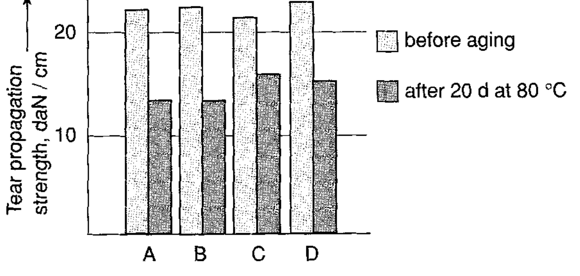


Figure 5.23 Tear propagation stength

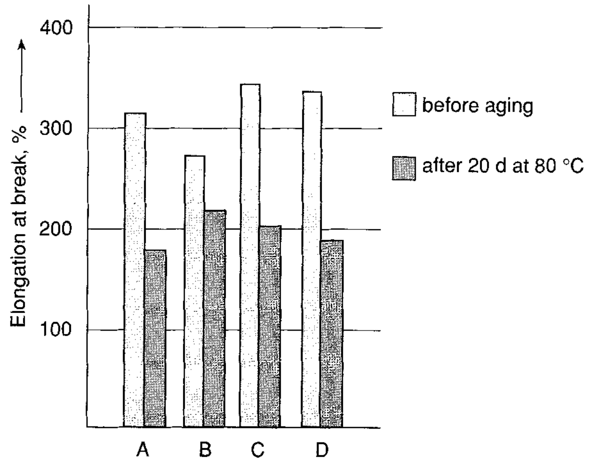


Figure 5.24 Elongation at break

The foregoing investigation is merely an indicative example based on SBR as the basic elastomer. In fact, tire makers mainly use rubber blends, depending on use, availability, and price. The proportion of resin may vary from ca. 2 to 20 wt % and depends on rubber type. For example, as natural rubber has high natural tack, less tackifier is needed compared with styrene-butadiene rubber. Resin proportion and type may also depend on the various additives incorporated, as well as on processing conditions.

5.5.2 Mechanical Rubber Goods

The application of rubber to form useful articles has its origin among the inhabitants of South America. This technology reached Europe in the eighteenth century. The first use was in the production of waterproof fabrics.

Apart from the tire industry, mechanical rubber goods include a wide variety of different products. Major users are the automotive and the footwear industries. Other uses are the manufacture of hoses, belts, gaskets, coatings, carpet backing, etc. Processing is mainly by molding, extrusion, or calendering.

Resins have a long history of use in rubber compounding, to facilitate compounding and to achieve suitable strength. The necessary properties are more or less the same as for the tire industry. Resins may also be used as cost-saving extenders. Resin concentrations are up to ca. 30 %, depending on the specific application.

The resin types used in rubber goods manufacture are the same as those used in the tire industry. For some special applications, light-colored or water-white resins are also of interest.

In contrast to the tire industry, manufacture of mechanical rubber goods is mainly carried out by smaller producers, often purchasing some or all of their stocks from custom compounders.

In connection with the manufacture of technical rubber goods, ethylene-propylene-diene terpolymers (EPDM) must be mentioned.

Comparatively little information is available on combinations of EPDM with hydrocarbon resins. Apart from natural and synthetic rubbers (e. g., SBR, NBR, CR, etc.) EPDM terpolymers have gained importance in polymer blends, focusing attention on which parameters relevant to rubber processing are influenced by resin addition.

Tentative tests of combinations with straight and modified C_9 resins have been carried out in filled and unplasticized, vulcanized and unvulcanized compounds. There is some indication of the following effects of resin addition

- Reduction in compound viscosity
- Improvement of scorch fastness
- Increase in ultimate elongation
- Improvement in tear resistance
- Compressive setting properties acceptable with respect to most requirements
- No significant effect on thermal degradation properties

5.6 Floor Tiles

In manufacturing floor tiles based on PVC or rubber, mostly SBR, a certain amount of hydrocarbon resins is currently used. These resins are mainly incorporated as processing aids, facilitating mixing and incorporation of fillers as well as calendering. Normally, all resin types may be used, including rosin and its derivatives and unreactive phenolic resins. Resin choice depends mainly on price, availability, and end use requirements (mainly color).

After World War II, large quantities of mainly indene-coumarone and aromatic petroleum-based resins were used in floor tile production for several decades. Nowadays, the volume of resins used in these systems is no longer very significant, although indene-coumarone and hydrocarbon resins still play a part in vinyl tile manufacturing in some countries as additional binder material.

It has also to be mentioned that rubber tile consumption is steadily increasing, e. g., for large surface coverings such as flooring in buildings. On the other hand, there is little or no increase in the market for PVC tiles, where asbestos fillers are being replaced by nonhazardous fibrous material.

Depending on the widely varying quality profile of floor tiles, the percentage of resins used as additional binder material may also vary, so that it is difficult to give a standard formulation. The following information merely lists a few main types.

A very low-cost floor tile can be produced from 65–70 % filler (mineral filler plus pigment) and a binder based on a mixture of 70 % resin and 30 % plasticizer. This formulation does not include any PVC. Here the resistance to alkali and saponification of the hydrocarbon resin is of prime importance, because floor coverings must be able to withstand washing with soap and scrubbing components.

However, floor tiles commonly consist of about 70 % filler and 30 % basic vinyl polymer or rubber which may either contain no resins at all or may include an admixture of

a suitable resin in a quantity of 10–30 % relative to the amount (30 %) of the basic polymer.

For the production of relatively dark-colored floor tiles, a normal indene-coumarone resin with softening point ca. 120 °C R&B is suitable. On the other hand, for the manufacture of light-colored floor tiles, normal indene-coumarone resins should not be used because of their tendency to yellow under the influence of light (UV), which may lead to discoloration of the finished tile. In that case, the use of either C_5 or C_9 resins (i. e., with zero or low indene content), or even water-white aromatic resins such as methylstyrene resins are suggested, because these resins have less tendency to yellow (see Section 4.2.12). The addition of UV stabilizers and/or antioxidants may also be beneficial.

While the use of cheap resins in PVC tile manufacturing originally motivated by the need to reduce manufacturing costs, resins lately gained importance as modifiers. One of the numerous PVC floor tile types, for example, is based on a manufacturing formula comprising styrene-modified indene-coumarone resins as an additional binder material. The use of this modified IC resin became a popular way to make standard floor tiles more resistant to indentation by the very high pressure excerted by stiletto heels. For this line of application, suitable IC resins with softening points of 100–120 °C R & B are modified with 7.5–15 % styrene to obtain copolymers with better indentation resistance (for more details see Section 3.5.1.1).

There is little information available on the modifications necessary for extrusion. Aromatic petroleum-based and indene-coumarone resins with softening points of ca. 100 °C R & B have been tested in the production of sheets made from hard or soft PVC. While a maximum of ca. 30 % can be added to the PVC, the quantity should be limited to ca. 10 %, otherwise the sheets become too brittle. Addition of the 100 °C R & B resin improves gelation of PVC, speeds up formation of the felt on the roller, and also improves mixing of the various components of the formulation.

The semiliquid indene-coumarone or aromatic petroleum-based resins with softening points ca. 30 °C R & B may also be used as plasticizers in PVC-based systems.

Because the selection of a resin depends on the basic polymer type used, as well as on the specific formulation and the required quality of the final product, manufacturers have to run their own preliminary tests to determine the optimum resin type and quantity to be used.

5.7 Foundry Industry

The foundry industry uses additives for different purposes: to bind the sand during casting, to prevent wetting of the molding media by the cast metal, and thus to produce a casting surface largely free of included sand grains. As a further positive side effect, they act as buffer materials, i. e., they create voids in the sand grain mass, enabling the sand grains to expand, thus preventing expansion defects. In organic-bound sand systems, these materials can also be used as breakdown agents.

Lustrous carbon formers are usually added to mechanically bonded sand (silica sand, bentonite mixtures, etc.). Lustrous carbon former additives to sand include a multitude of products, e. g., coaldust, pitch, bitumen, synthetic materials (polyethylene, polystyrene), oils, and mixtures of any of these materials. Of these materials, resins play an important

part. Further buffer materials can be added (for example, peat). Alternatively, the addition of materials such as clays and bentonite can be employed in order to assist the grinding of the carbon materials.

5.7.1 Hydrocarbon Resins as Lustrous Carbon Formers

The lustrous carbon former molding media additives have been in use for a comparatively short time. Increasing importance is therefore given to pitch, resins, and synthetic materials and mixtures of these. Experience gathered over a number of years has shown that indene-coumarone and aromatic petroleum-based resins are particulary suitable as lustrous carbon formers, owing to their high carbon content. These resins are noted for their neutral character: they are unsaponifiable, stable against alkaline or acid conditions, and chemically inert. They have very good thermal and electrical insulation characteristics, as well as excellent properties as lustrous carbon formers.

Use of these resins has the following advantages:

- Very high lustrous carbon producing capability
- Advantageous sequence of the lustrous carbon formation
- Very low smoke emission
- Very low ash content, and hence a reduction of dust (fewer casting defects); because of the reduced fines, a saving in bentonite addition is also achieved
- Very good mulling properties

Most of the lustrous carbon formers employed provide lustrous carbon values of 25–25 %, but values > 60 % have been measured for indene-coumarone and aromatic petroleum-based resins. From an ecological point of view it is important to note that lustrous carbon formers such as coaldust, produce considerable amounts of smoke at temperatures as low as 200 °C, whereas these resins produce very little smoke in this temperature range, i. e., lustrous carbon formation can take place without a prior "smoke phase".

5.8 Resins as Mineral Oil Additives

Addition of hydrocarbon resins, especially of the aromatic type, to mineral oils allows one to adjust the rheological properties of an oil to a required specification. As aromatic petroleum-based and indene-coumarone resins are neutral and unsaponifiable, and show good heat resistance, they are particularly suitable as mineral oil additives, e. g., in the printing ink and rubber industry. Their good dielectric properties also make them useful components in formulating cable oils, insulating cable jointings, and related applications.

Resin solubility and resulting oil rheology are the most important physical characteristics of oil/resin blends. Aromatic hydrocarbon resins are added to mineral oils to increase oil viscosity. Evidently, there is a direct dependence of the resulting viscosity on resin solubility, i. e., on the chemical characteristics and softening point.

Solubility of an aromatic resin is better in mineral oils with a higher aromatic content, or in predominantly naphthenic oil types than in more paraffinic mineral oils.

To find a resin/oil blend with satisfactory performance, the compostion of the mineral oil must first be determined. The solubility of the added resin in the mineral oil of known composition, must also be determined. Depending on the composition of the basic mineral oil, different viscosities can be obtained for the same proportion of resin. The viscosity increase is steeper the higher the softening point of the resin, and vice versa. From experience, it can be stated that the viscosity of an oil/resin blend is always higher when the solubility of the resin in the oil is in the borderline range. Therefore, two principles should be observed when formulating oil/resin blends:

- the resin must be sufficiently soluble to avoid phase separation and precipitation, sometimes even at low temperatures
- the resin type (chemical composition and softening point) must be selected so that solubility is sufficient, preferably near the borderline to ensure a marked or steep increase with the lowest possible quantity added

By these variations almost any rheological profile of a mineral oil can be achieved.

Because of the above outlined manifold correlation possibilities it is rather difficult to suggest any specific formulations. In general terms, it is necessary to determine in each case which specific resin type is best suited, taking into consideration the solubility in the mineral oil and the viscosity to be achieved.

However, when the exact mineral oil type and the required viscosity range is known, resin suppliers are able to suggest an appropriate resin type, the optimal softening point, and addition quantity.

Frequently suggested resin types, depending on specific requirements, are:

- C_9 resins with relatively high indene content
- C_9 resins with high α-methylstyrene/vinyltoluene content
- C_4-modified indene-coumarone resins
- C_4-modified C_9 resins
- C_9 resins with high methylindene content

The mineral oil solubility of these resin group increases and the solution viscosity decreases in the sequence listed above, a further demonstration that the viscosity increase is steeper with a somewhat lower degree of solubility, and vice versa.

It is frequently suggested that one should run preliminary tests with resins of softening point ca. 100 °C R & B, and subsequent tests with higher melting resins to find the most appropriate resin to obtain the required viscosity.

C_9 resins with a relatively high content of α-methystyrene/vinyltoluene are used in mineral oils with high naphthenic content or in aromatic containing oils. C_9 resins with a higher methylindene content, because of their different solubility characteristics, can also be used in more critical mineral oils, i. e., with a lower naphthenic content. The same is true for C_4-modified C_9 hydrocarbon resins.

It should be noted that standard C_5 hydrocarbon resins are generally not so well suited for blending with mineral oils to increase viscosity. This is due to their excellent oil solubility, resulting in a low solvent viscosity. This cannot be compensated by higher melting point resins, because they are mostly not available among the standard C_5 resins.

Resins in printing ink oils and oils in rubber compounding have attracted great interest in recent years. There is increased public awareness of the extent to which some oil-derived chemicals pose a health rist. In the light of legislation and evironmental regulations, some

oils are considered dangerous, or at least suspect, because they contain certain carcinogenic aromatic compounds. A typical example are the so-called aromatic oil extracts, widely used in printing ink manufacture, and as processing aids in rubber compounding.

For these reasons, producers of ink oils and processing oils have sought to replace the environmentally suspect aromatic oil extracts.

Nonhazardous mineral oils, for instance hydrogenated naphthenic oils, have been considered as an alternative. However, they fail to satisfy some important requirements. The major problems are the generally low viscosity, and the lack of aromaticity.

Recent work has shown that liquid and semisoft indene-coumarone resins and/or C_9 hydrocarbon resins are suitable for correcting viscosity and for enhancing aromaticity. Depending on solubility and process conditions, solid resins can also be used.

As the development of suitable substitutes for aromatic oil extracts is relatively new, little information is generally available. It is extremely difficult to suggest generally applicable formulations, especially since the replacement oil may be used in quite different fields, and even within these areas the specific requirements may be quite diverse.

In the rubber industry, it is the aromaticity which needs to be markedly increased in the mostly naphthenic or naphthenic/paraffinic substitute oils. In some cases, the viscosity must be increased by resin addition from ca. 250 to ca. 800–1 000 mPa·s. The resin types suggested are liquid indene-coumarone resins or blends of these liquid resins with 30 °C R & B semisoft resins.

For printing oils, a markedly increase of aromaticity is very important. Regarding the rheological properties, the ink industry requires oils with much higher solvent viscosities. Table 5.10 gives a typical example.

Table 5.10 Viscosity requirements for printing oils

	Paraffinic/naphthenic starting oil (cylinder oil 302)	Alternative product (data required)
Aromatic carbon, %	17	40
Viscosity at 20 °C, mPa·s	9 200 ± 200	10 000–13 000
Aniline point, °C	102	40

By varying the ratio of liquid and 30 °C R & B indene-coumarone resins, and by adding 50 % to a cylinder oil, a viscosity of 10 000–13 000 mPa·s at 20 °C can be achieved, suitable for ink manufacture purposes.

Other suitable mixtures using higher melting resin components are given in the suggested formulations below (approximate figures only):

– C_9 resin with high indene content, 150 °C R & B	25 %
– Naphthenic mineral oil, hydrogenated	75 %
– Viscosity at 20 °C	1 300 mPa·s
– C_9 resin with high indene content, 150 °C R & B	35.5 %
– Oil as above, high viscosity	64.5 %
– Viscosity at 20 °C	22 500 mPa·s

It should be mentioned that in some cases the ink oil industry is interested in resin oil blends showing a viscosity increase, from 9 000 to about 30 000 mPa·s/20 °C. This can only be achieved with extremely high softening resins, but there is the risk of insufficient oil solubility and/or oil tolerance. Solubility of very-high-melting resins improves with lower oil viscosity (low boiling range) and increased aromatic content. This problem may be overcome by selecting appropriate oil blends, or by the use of C_5/C_9 resin blends with sufficiently high softening points, if available.

Some additional remarks on the subject of oil/resin blends for the ink industry are worth making. A high concentration of aromatic carbon (> 30 %) is associated with good pigment wetting properties, an important factor. Further adjustment of viscosity and incorporation of extra additives usually require a high aliphatic tolerance. Modification of a rather high-resin solution (ca. 35 %) in a naphthenic oil can be achieved by adding an appropriate quantity of linseed oil to give the desired tack and swiftness (stringiness).

A solution of a high-melting resin in a lower-viscosity mineral oil speeds up absorption of the ink by the substrate in rotary offset systems. Table 5.11 shows some comparative figures for resin content, viscosity, aliphatic tolerance, and content of aromatic carbon for some resin/oil blends with indene-coumarone resins with a high indene content and aliphatic (DCPD)/aromatic resin types.

Table 5.11 Properties of resin/oil blends

Mineral oil		Resin				
Type*	Quantity %	Soft. pt. °C R & B	Quantity %	Viscosity mPa·s/ 20 °C	Aliphatic tolerance	Aromatic carbon
High-indene resins						
A1 800	60	155	40	12 100	11	33
A1 800	64	165	36	12 300	4	31
B1 800	60	155	40	12 700	14	35
B1 800	64	165	36	12 000	7	33
B2 230	89	155	11	12 100	18	25
Aliphatic (DCPD)/aromatic resin						
A1 800	61	150	39	12 100	4	15
B1 800	61	150	39	12 600	5.5	18
B2 230	89.5	150	11.5	12 200	6	21

* A = hydrotreated naphthenic; severe hydrogenation; 17 % aromatics
B = hydrofinished naphthenic; low severity hydrogenation; 25 % aromatics

Finding a resin/oil blend which is entirely satisfactory in all respects is not easy. The end user generally has to settle for a compromise. This is easily deduced from the following:

- to impart a high viscosity to a low-viscosity oil requires a very high-melting resin
- a high-melting resin increases the viscosity more steeply than a lower-melting resin

- a higher-melting resin has a lower oil solubility and a lower aliphatic tolerance
- the higher melting the resin, the lower the amount to be added
- aliphatic resins have better oil solubility and good aliphatic tolerance
- softening points of standard aliphatic resins are not high enough to increase the oil viscosity substantially

Demands on the resin/oil blend are often contradictory to the chemical and physical characteristics of the oil or the resin. The effects that can be achieved depend, as has been shown, on finding the optimal chemical properties and softening point of the resin to be blended with a given oil of given composition. On the other hand, good effects can be obtained when it is possible to find an appropriate oil composition for a resin with given characteristics and softening point. This is the major difficulty in developing an optimal solution for a specific problem in formulations.

5.9 Miscellaneous Uses

5.9.1 Chewing Gum Base

The gum base material can be either natural gum or synthetic (e. g., polyisobutene). Resins are used as plasticizing additives. The authorized additives are specified by the Food and Drug Administration and other national authorities.

Widely used additives are natural terpene resins and synthetic polyterpene resins. Indene-coumarone and some petroleum-based hydrocarbon resins have been used in chewing gum base for a very long time, but are no longer listed as approved substances by the FDA.

5.9.2 Investment Casting

This ancient process, also known as the lost wax process, is used to cast small precision metal parts. Recently there seems to have been a resurgence of the process.

This technology uses wax blends (paraffin wax/microcrystalline wax) to which resins are added. The wax/resin ratio is normally ca. 1 : 1. The added resin has both tackifier and filler functions. The resin types used should possess thermal stability, low melt viscosity, and good wax compatibility.

In the investment casting process, a wax/resin blend is melted and cast or injected into the mold. After the solidified blend is removed from the mold, a thermosetting ceramic material is cast around the wax/resin blend pattern and cured. The pattern is then melted and removed, leaving a high-precision mold.

The resins mostly used are aliphatic C_5 resins, but aromatic C_9 resins (and some C_5/C_9 hybrid resins) are also suitable. Rosin esters are also fairly common. The wax-compatible

C_5 resins are primarily used as tackifying binders, whilst the less wax-compatible aromatic C_9 resins or hybrid types act as fillers.

It should be mentioned that the process has recently been applied to jewelry production.

5.9.3 Ceramic Industry

In a mixture of powdered ceramic material and other additives, hydrocarbon resins can serve as binder material, as preliminary experiments have shown.

The mixture is applied in injection molding of ceramics. In a prebaked process the resin is pyrolized. The remaining carbon framework holds together the prebaked mass, which subsequently passes through the actual baking process, i. e., the resin serves as binder in making "green" molded article precursor. The odor from the desintegrating resin, noticeable during the prebaking process, may prove to be a problem.

The binder materials mostly used are phenolic resins and coal-tar pitches.

5.9.4 Textiles

In textile treatment and waterproofing, special hydrocarbon resins, such as α-methystyrene/vinyltoluene or C_5 resins, may be used to retexture and waterproof textiles after dry-cleaning. This application seems now to be largely dominated by other products, e. g., acrylics or silicones.

5.9.5 Gypsum Waterproofing

Gypsum is extensively used in the construction industry for interior finishing by manual application, or in industrially prefabricated panels. For exterior use or special humidity-resistant applications, gypsum is normally not suitable because of its sensitivity to humidity. Utilization of aromatic hydrocarbon resins in the form of an aqueous emulsion increases the water resistance of gypsum preparations. For example, gypsum prepared with a resin emulsion (45 % dry material, 5 % resin to gypsum), dried at 30 °C, after 25 min immersion in water at 20 °C absorbs ca. 1.5 % of its weight, whereas untreated gypsum absorbs ca. 45 % of its weight.

Hydrocarbon Resins
R. Mildenberg, M. Zander & G. Collin

6 Chemical Compositions and Resin Selection

In Chapter 4, it has been explained that the general properties of a resin depend in the first place on the type of feedstock (e. g., C_9, C_5, or DCPD). Knowledge of the raw material alone may suffice for resin selection in some applications. For more specific fields of application, selection of the most appropriate resin may depend not only on the feedstock origin, but also on the detailed chemical composition of the resin.

In the following, it will be shown that certain resin constituents or groups of constituents can have a bearing on the performance of the resin type.

In the manufacture of C_5 resins, the nature of the olefins, and the ratio of mono- to diolefins in the feedstream (see Section 2.2.2) are important for the properties of the final resin, e. g., the higher the monoolefin content the higher the solubility, and the lower the monoolefin content the higher the resin hardness.

In the production of dicyclopentadiene resins, the properties can be influenced by the choice of comonomers of aliphatic or aromatic type, e. g., feeds containing styrene or indene allow manufacture of resins with high softening points.

For a detailed description of the various correlations, feedstreams of indene-coumarone and C_9 type were chosen. The latter type was chosen for discussion because the rather wide latitude in special resins made from partial cuts of the C_9 feedstock provides a particularly simple demonstration.

First of all, the gas chromatograms shown in Chapter 2 must be recalled (Figs. 2.5–2.7). For easier understanding, the GLC scans shown in Figures 6.1 and 6.2 are presented in very simplified form.

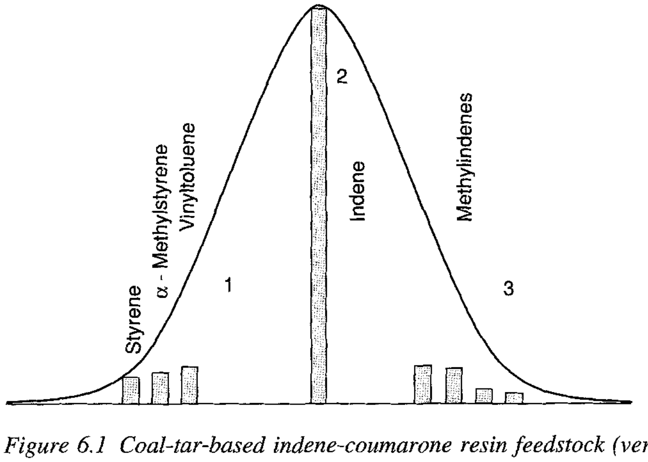


Figure 6.1 Coal-tar-based indene-coumarone resin feedstock (very simplified GLC scan)

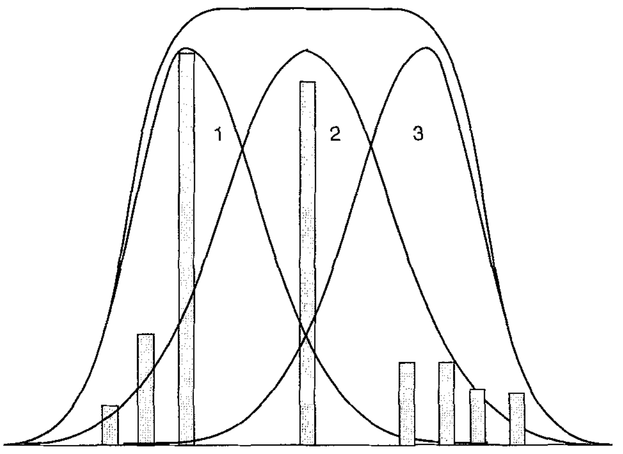


Figure 6.2 Petroleum-based C_9 resin feedstock (very simplified GLC scan)

The first use of these schematic GLC scans is to identify the most important physical and chemical characteristics with the single resin constituents or groups of components from which they may be manufactured. Although this can only offer a rough approach, the simplified scans, in combination with Table 6.1, can be instrumental in selecting the most appropriate resin for a particular end use.

6.1 Indene-Coumarone Resins

IC resin feedstocks and the respective resins contain only very small quantities of styrene/α-methylstyrene/vinyltoluene (1) and also small quantities of methylindenes (3). By far the most dominant component is indene (2). The resin-forming feedstock from coal tar with this high concentration of indene does not offer any commercially feasible possibility for variation, i. e., to make partial cuts of this fraction. This means that the characteristics of the indene solely determine the possible use for this resin type. As no variables with special features are feasible, there is little choice in this resin line, i. e., straight indene-coumarone resins are selected only on the basis of their color and hardness (softening point).

6.2 C_9 Hydrocarbon Resins

As already explained in Section 2.2.1, the individual constituents of C_9 resins are identical with those of indene-coumarone resins, but the percentage distribution is quite different as there are substantial quantities of styrene/α-methylstyrene/vinyltoluene (1) and methylindenes (3) as well as indene (2).

This allows more possibilities for variation, i. e., to make partial cuts around different groups of constituents. It is therefore feasible to make resins with different characteristics from C_9 feedstocks. In Table 6.1 important properties of resins made from three partial cuts are listed:

Table 6.1 Special features of resins from partial C_9 cuts

Group of constituents	Prominent features	Other features
1 Styrene/α-methylstyrene/vinyltoluene	light color, good thermal stability, good light stability	medium compatibility and solubility, toughness, medium to high solvent and melt viscosity
2 Indene	high hardness, medium to low light stability	relatively high solvent and melt viscosity
3 Methylindenes	excellent solubility and compatibility	low solvent and melt viscosity, medium to low thermal stability, low light stability

It must be noted that the features mentioned are not a complete list; they are given merely to distinguish the major properties which may vary to some degree, for instance, with the melting point.

Resins made from the complete, unfractionated raw material feedstream have characteristics which are essentially combinations of the individual physical and chemical properties listed in table 6.1. The resin exhibits an overall property mix with no extremes or particularly accentuated features. This type of resins meets most quality requirements in the various fields of application. For customers with special requirements regarding one or more prominent features, a resin made from the complete fraction may not be entirely satisfactory, and resins made from cuts or combination of cuts may be a better choice.

Although some companies offer pure polymers or blends of pure polymers, mostly in the higher price range, it is often sufficient to select resins made from partial fractions with a strong emphasis on one of the groups 1–3 referred to in Table 6.1. These resin types are offered by many resin producers in addition to their standard resins.

A few simple illustrative examples are given below:

• Rubber industry
Requirements: no particular property emphasized
Suggested type: standard resins

• Paints/lacquers
Requirements: low color, good light stability, low solvent viscosity
Suggested type: group 1

• Adhesives/woodworking hot-melts
Requirements: high hardness, good thermal stability, good compatibility (e. g., with ethylene-vinylacetate copolymers)
Suggested type: combination of group 2 with varying portions of group 1 and/or group 3, depending on the particularly emphasized property (i. e., thermal stability: 1 + 2; compatibility: 2 + 3)

It is clear that in many cases one has to compromise, as can be seen in the properties listed in Table 6.1. However, it should be taken into account that most customers use a variety of components in their formulations, allowing adjustment and optimization by adding other resins, oils, solvents, plasticizers, stabilisers, antioxidants, etc.

In connection with the above it is worth mentioning that similar deliberations concerning special features offered by resins from special cuts are also possible for C_4-modified C_9 hydrocarbon resins. For example, they can substitute the resins of group 3, because of their overall excellent solubility and compatibility.

Concluding this chapter, it is suggested to keep in mind the schematic GLC scan of a C_9 hydrocarbon resin oil (or resins made thereof) and the corresponding table of the most prominent properties of the final resin; this gives only a rough guide, but is often useful. It is also worth stressing that a vital factor in the development of many special resin types is close cooperation between customer and the resin producers.

6.3 Comparison of Competitive Resins

In many cases the question "which resin is equivalent to resin X?" cannot be easily answered. Strictly speaking, there is no equivalent unless the comparable resin is manufactured from exactly the same feedstock by the same technology. The answer can only be "resin A comes close to the characteristics of resin X".

Another even more important factor is exact knowledge of the purpose for which the resin is going to be used, and in combination with what solvent and/or other components (resins, elastomers, etc.). If a resin type is selected simply by checking the physical characteristics (softening point, color, aromatic, aliphatic, etc.) the appropriate resin may in fact be of a quite different type if the exact area of application had been known before selecting. Even if a resin only comes close to the characteristics of the competitor resin, or if there is no real equivalent, this does not necessarily mean that an available resin may not do the job as well as the competitor. In many cases, more than one resin type may be appropriate.

A difficulty is that sometimes there may be little information on the real physical/chemical characteristics of the competitor resin. The published information may be vague or even misleading. For instance, resins are described as alkylated resins. This may mean resins which are intentionally alkylated in the real sense of the word (i. e., basic material stream plus an alkyl component). However, it can also mean that in the course of polymerization of the raw material (with no added alkyl component), both polymerization and alkylation products have been formed.

In other cases, one and the same resin is offered under separate names for different fields of application, and sometimes under different names in different countries.

The main difference in competitive resins can be traced back to the raw materials. The resin can be based on fractions from coal tar (IC resins), on petroleum-based fractions (for C_5 or C_9 resins) etc. Though the feedstocks for these resins are different, the manufactured resin types may still be applicable in exactly the same field, but may differ in performance.

A more difficult problem remains: the customer may just check the physical data of the sample without giving much thought to whether another resin may not serve the same purpose as well. A typical example is the selection of resins for the rubber industry (see

Section 5.5). Almost every type of resin is used in rubber formulations, although in many cases they are quite different in chemical structure (IC, C_9, C_5, DCPD).

In consideration of these points it is good advice that whenever a potential customer is seeking an alternative resin, as much as possible should be known to the resin supplier about the intended end use. This not only helps in making a proper selection, but may also offer a chance to give appropriate hints and additional information on the characteristics of the resins and their possible benefits for the particular application.

In any case, it is imperative that the customer really tests the suggested resin to find out whether it will do the expected job in the particular formulation.

Hydrocarbon Resins
R. Mildenberg, M. Zander & G. Collin

7 Quality and Quality Assurance

Customers are more and more insisting on quality, consistency, and reliability, This demand was initiated in the early 1980s by the Japanese automotive industry, and is now generalized worldwide (ISO 9000).

The traditional view of quality consisted in determining a quality standard economically, and in accordance with the manufacturing companies interests. Conformance with the defined quality level is achieved by inspection and testing of the finished product, and elimination and/or rework of defective material.

The new aspect of quality is to prevent defects from occuring. The slogan is "do it right first time". Concern with quality must be a whole concept, including all parts of a company, the entire manufacturing operations, and services. Quality must be the company philosophy – a corporate culture –, and an essential part in the competitive strategy. Motivation must come from the top management.

To assure correct product manufacturing, the production process must be controlled to detect causes of failure. A method to do this is Statistical Process Control (SPC). This means, monitoring and control of the production process at every stage to assess the degree of conformance of raw material, process, and product to previously agreed specifications. SPC is a technique of monitoring those data against statistically derived limits.

Usually, the comparison is made on control charts, which allows to show if the process is in or out of control. If a given process parameter is out of control, appropriate action is

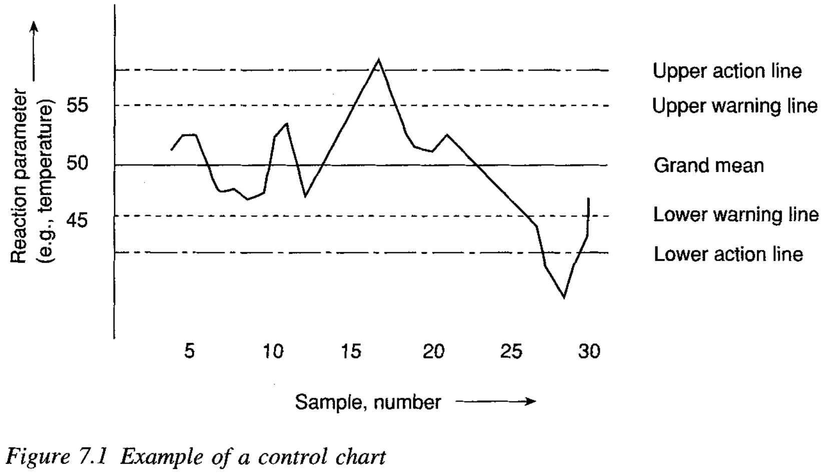


Figure 7.1 Example of a control chart

taken to bring the process into control. A general example of a chart is given in Figure 7.1.

It is not within the scope of this book to go further into details of quality assurance and control. General lines are only mentioned very simplified to attract the reader's attention to those tendencies (see also literature [7.1-7.4]).

Hydrocarbon resin manufacturers are more and more involved in applying quality assurance policy in close collaboration with the customers.

Hydrocarbon Resins
R. Mildenberg, M. Zander & G. Collin

8 Toxicology and Legal Aspects

Legislation concerning the use of hydrocarbon resins is regulated by many national authorities, but will likely be harmonized with the requirements of the FDA (United States) and the European Community. The main questions are directed to the migration of monomers, oligomers, and additives that might contaminate contiguous media by diffusion, and to the stability of resin formulations under the conditions applied.

A great number of hydrocarbon resins are approved substances as defined in the Food and Drug Administration Regulations (FDA Status) for the following:

175.105:	Adhesives
175.300:	Resinuous and polymeric coatings
176.170:	Components of paper and paperboard in contact with aqueous and fatty foods
176.180:	Components of paper and paperboard in contact with dry food
177.1210:	Closures with sealing gaskets for food containers
177.2600:	Rubber articles intended for repeated use
178.3800:	Preservatives for wood

Regarding the health hazards of many hydrocarbon resin types, it is known that acute oral toxicity in rats (LD_{50}) is greater than 10 g/per kilogram body weight. Skin and eye irritation tests indicate a very low order of toxicity. Within the EEC directives, many hydrocarbon resins are not classified as harmful or toxic, nor irritant to skin and eyes.

Industrial experience has shown that most hydrocarbon resins can be processed without hazard to personnel, providing the usual precautions for handling chemicals are observed. Precautions should be taken against inhalation of dust or fumes by using respiratory masks in confined areas, and maintaining adequate ventilation.

If these substances enter the eye, the standard procedure is to bathe well with plenty of water; in the case of skin contact, washing with soap and water is recommended. Soiled clothes should be laundered before being reworn.

With regard to emergency action, it is suggested that fires involving resins should be extinguished with powder, foam, or carbon dioxide appliances. A Safety Data Sheet for a standard resin is illustrated below:

Safety Data Sheet
According to 91/155 EC

Printing date 26. 09. 95 Reviewed on 29. 07. 94

1 Identification of substance:
Product details:
Trade name: XXX C_9 Hydrocarbon resins, softening point range 90–150 °C R & B
Manufacturer/Supplier:
Information: Product safety department.
Emergency information: see: manufacturer/supplier

2 Composition/Data on components:
Chemical characterization:
CAS No. Designation:

71302-83-5 Hydrocarbons, C_9-unsaturated, polymerized
Identification number(s): void (Polymer)

---

3 Hazards identification:
Hazard designation: void

---

4 First aid measures:
General information: No special measures required.
After inhalation: Supply fresh air; consult doctor in case of symptoms.
After skin contact: Clean affected area with soap and plenty of water.
After eye contact: Rinse opended eye for several minutes under running water.
After swallowing: In case of persistent symptoms consult doctor.

---

5 Fire fighting measures:
Suitable extinguishing agents: Use fire fighting measures that suit the environment.
Protective equipment: No special measures required.

---

6 Accidental release measures:
Person-related safety precautions: Not required.
Measures for environmental protection: No special measures required.
Measures for cleaning/collecting: Collect mechanically.
Additional information: No dangerous materials are release.

---

7 Handling and storage:
Handling:
Information for safe handling: No special measures required.
Information about protection against expolosions and fires: No special measures required.

Storage:
Requirements to be met by storerooms and containers: No special requirements.
Trade name: XXX C_9 Hydrocarbon resins, softening point range 90–150 °C R & B

Information about storage in one common storage facility: Not required
Further information about storage conditions: None.

8 Exposure controls and personal protection:
Additional information about design of technical system:
No further data; see item 7.
Personal protective equipment:
General protective and hygienic measures:
The usual precautionary measures should be adhered to general rules for handling chemicals.
Breathing equipment: Not required.
Protection of hands: Not required.
Eye protection: Not required.
Body protection: Protective work clothing

9 Physical and chemical properties:
Form: Solid
Colour: Yellow-brown
Odor: Weak, characteristic

	Value/Range	Unit	Method
Change in condition:			
Fusion temperature/range:	85–145	°C	ASTM D3461
Flash point:	> 200	°C	DIN ISO 2592
Ignition temperature:	> 450	°C	DIN 51 794
Decompostion temperature:	> 250	°C	

Self-inflammability:	Product is not selfigniting.		
Danger of explosion:			
Dust can form explosive mixtures with air			
Critical values for explosion:			
Lower:		15 g/m³	
Vapour pressure:	at 20 °C	< 0.2 mbar	DIN 51 754
Density:	at 20 °C	1.06–1.11 g/cm³	DIN 52 004
Solubility in/Miscibility with			
Water:	Insoluble		

10 Stability and reactivity:
Thermal decomposition/conditions to be avoided:
No decomposition if used according to specifications.

Dangerous reactions: No dangerous reactions known

Dangerous products of decomposition:
No dangerous decomposition products known.

11 Toxicological information:

Acute toxicity:

Specific symptoms in biological assay: LD50 (oral-rat): < 16 000 mg/kg

Primary irritant effect:

on the skin: No irritant effect.

on the eye: No irritant effect.

Sensitization: No sensitizing effect known.

Additional toxicological information:
When used and handled according to specifications, the product does not have any harmful effects according to our experience and the information provided to us.

12 Ecological information:

Ecotoxical effects:

Remark: Can be mechanically separated in sewage purification plants.

General notes:
Water hazard class 0 (German Regulation); (Self-assessment): generally not hazardous for water.

13 Disposal considerations:

Product:

Recommendation:
Remove according to local authority recommendations, e. g. convey to a licensed incinerator.

Uncleaned packagings:

Recommendation:
Disposal must be made according to official regulations.

14 Transport information:

Transport/Additional information:
No dangerous good according to international transport regulations.

15 Regulatory information:

Designation according to EC guidelines:
Labelling according to EEC Directives/Ordinance on Hazardous Substances (GefStoffV) is not required.

16 Other information:
This data is based on our present knowledge. However, it shall not constitute a guarantee for any specific product features and shall not establish a legally valid contractual relationship.

Department issuing data specification sheet:
Product safety department.

9 Economic Aspects

In a great number of industries, e. g., adhesives, rubber, paint, and printing inks, hydrocarbon resins play an important part in specific formulations. In most fields of application, these resins are not used as the sole base substance, but in combination with other materials, to supply, modify, or enhance certain product properties, or they may be used as processing aids.

Although hydrocarbon resins have been commercially available for more than 90 years, there is still an increased demand for standard and/or special types. Present total manufacturing capacity is sufficient to meet immediate and medium-term demand. Total capacity for synthetic hydrocarbon resin production is estimated to approach 10^6 t/a worldwide, with the main capacities located in the United States, Europe, and Japan. Hydrocarbon resins are also produced in Brazil, Canada, China, India, Korea, Russia, and Taiwan.

An estimated breakdown by geographical zone and resin type is given in Table 9.1.

Table 9.1 Estimated capacity and production of hydrocarbon resins (1995)

Geographic zone and resin type*		Capacity, kt	Production, kt	Use, %
America				
	A	160	145	90.6
	B	190	145	76.3
	C	70	65	92.8
		420	355	
Europe				
	A	80	70	87.5
	B	120	100	83.3
	C	45	40	88.8
		245	210	
Asia/Pacific:				
	A	75	65	86.6
	B	180	90	50.0
	C	40	35	77.8
		295	190	
Worldwide		960	755	78.6

* A = C_5 hydrocarbon and DCPD resins
B = Indene-coumarone and C_9 petroleum-based resins
C = Water-white hydrocarbon resins

A breakdown of world production by resin type is given in Table 9.2.

Table 9.2 Breakdown of resin production by type

Resin type	Production, kt	%
C_5 and DCPD resins	ca. 280	37.1
IC and C_9 resins	ca. 335	44.4
Water-white resins	ca. 140	18.5
	755	100

Additional manufacturing capacity for hydrogenated, water-white resins and some C_5/C_9 hybrid resin types is scheduled to go on stream in 1996/97.

The price of hydrocarbon resins depends in the first place on the general trend of ethylene steam-cracker feedstock costs, and is very difficult to forecast because of the many factors involved.

Table 9.3 Resin manufacturers and trade names

	Trade names	Resin types
Europe		
Akzo (Netherlands)	Setalin	hydrocarbon-modified phenolic resins
Cray Valley (France)	Norsolene	C_9 and C_5–C_9 resins
DRT (France)	Dercolyte, Dertophene	terpene and modified terpene resins
DSM (Netherlands)	Uratak	C_9 and phenol-modified C_9 resins
Exxon (France)	Escorez	C_5 and C_5–C_9 resins; DCPD and hydrogenated DCPD resins
Hercules (Netherlands)	Hercures, Regalite, Kristalex, Hercoflex	C_5 and C_9 resins, C_5-C_9 resins, resins from pure monomers, hydrogenated resins
Hoechst (Germany)	Karboresin	modified hydrocarbon resins
NEVCIN (Netherlands)	Necires, Nevchem, Nevex, Nevbrite, Nevroz, Nevillac	C_9 and C_5-C_9 resins, DCPD and modified DCPD resins, phenol-modified resins
VFT AG (Germany)	Novarez	C_9 and modified C_9 resins, IC and phenol-modified IC resins
United States		
Amoco	Amoco resin 18	poly(α-methylstyrene)
Arizona	Zonarez, Zonatac, Newtac, Nirez, Sta-Tac, Betaprene, Beta-Tac	terpene and modified terpene resins, C_5 and DCPD resins

Table 9.3 (continued)

	Trade names	Resin types
Chemfax	Stygene, Chemprene, Pentaprene, 5 AM	C_9 and IC resins, DCPD resins
Eastman	Eastotac	C_5–C_9 resins, hydrogenated resins
Exxon	Escorez	C_5, C_5–C_9, and C_9 resins, hydrogenated resins
Goodyear	Wingtack	C_5 and C_5–C_9 resins
Hercules	Adtac, Piccodiene, Piccopale, Picotac, Piccovar, Hercotac, Picco, Regalrez, Piccolastic, Kristalex, Piccotex, Piccolyte, Piccofyn, Endex	C_5, C_9 and DCPD resins, terpene and modified terpene resins, resins from pure monomers, hydrogenated resins
Lawter	Pertro-Rez, Alpha-Rez	C_9 and modified C_9 resins, DCPD and modified DCPD resins
Neville	LX, Paradene, Nevilac, Nevchem, Nevoxy, Cumar, Nevex, Nevpene, Nevroz, Nebony, Nevtac	IC resins, C_5, C_9, C_5–C_9, and modified DCPD resins
Polysat	Polysat LC	modified C_9 resins, DCPD and modified DCPD resins
Resinall	Resinall	C_9, modified C_9, and modified DCPD resins
Sartomer	Norsolene	C_9 and modified C_9 resins
Schenectady	SP	terpene-phenolic resins
Sunbelt	Sunresin	C_5, C_9, and modified C_9 resins, modified DCPD resins
Japan		
Arakawa	Arkon	hydrogenated resin
Idemitsu	Admaru	styrene resins, DCPD resins, hydrogenated resins
Maruzen	Marukarez	C_5 and DCPD resins, hydrogenated C_5 and DCPD resins
Mitsui	Hi-rez, Petrosin, FTR	C_5 and C_9 resins, resins from pure monomers
Nippon Petrochemical	Nisseki Neopolymer	C_9 resins, liquid resins
Nippon Steel	Nittetsu	IC resins
Nippon Zeon	Quintone	C_5 and modified C_5 resins, DCPD and modified DCPD resins
Toho	Hiresin, Coporex	C_5–C_9 resins
Tonen	Escorez	C_5, C_9, C_5–C_9, and DCPD resins, hydrogenated DCPD resins
Tosoh	Petcoal, Petrotack, Corplex	C_9 and C_5–C_9 resins
Yasuhara	YS, Polystar, Clearon	terpene, modified and hydrogenated terpene resins

Table 9.3 (continued)

	Trade names	Resin types
Other countries		
Canada St. Lawrence	Salar, Arotac, Coumin	C_9 and IC resins, DCPD resins
Brazil Petroquimica	Unilene	C_9 resins
Korea Kolon	Kolon	C_5, C_9 and IC resins
Taiwan Yung Tung	Sunrez	C_9 resins
India Indian Petrochemical Corp.	Petrez	C_9 resins

Hydrocarbon resins are also manufactured in China, Bulgaria, Poland, and Russia.

References

General References

G. Collin, R. Mildenberg, M. Zander: "Resins, synthetic" in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A23, pp 89–108, VCH Verlagsgesellschaft mbH, Weinheim, 1992

M. Vredenburgh, K. F. Foley, A. N. Scarlatti: "Hydrocarbon Resins" in Encycl. Polym. Sci., Vol. 7, pp 758–783, John Wiley, New York, 1987

J. F. Holohan, Jr., J. Y. Penn, W. A. Vredenburgh: "Hydrocarbon Resins" in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 12, pp 852–869, Wiley Interscience Inc., New York, 1980

H.-G. Franck, G. Collin: "Steinkohlenteer", pp 92–95, 162–169, Springer Verlag, Berlin, Heidelberg, New York, 1968

References for Chapter 2

[2.1] G. Krämer, A. Spilker: Chem. Ber. 23 (1890), pp 78 and 3276; 33 (1900), p 2257

References for Chapter 3

[3.1] J. P. Kennedy, E. Maréchal: "Carbocationic Polymerization", pp 10–12, John Wiley, New York, 1982

[3.2] M. Prillieux (Esso Chimie), Pétrole et Techniques, No. 268, pp 44–45 (1980)

References for Chapter 4

[4.1] E. R. Ruckel, H. G. Arlt, Jr: Naval Stores Rev., Jan.-Feb. 1984, p 6

[4.2] E. R. Ruckel in "Carbocationic Polymerization (see [3.1])

[4.3] M. Prilleux, Pétrole et Techniques, No. 268, p 43

[4.4] A. Taketa, Chem. Economy and Eng. Rev. 8 (1976), p 29

[4.5] "Mettler F 9800 Thermosystem", Techn. Paper

[4.6] Transition Temperatures of Polymers by Thermal Analysis, ASTM D 3418

[4.7] G. L. Brown, "Resins in Rubber", Pennsylvania Industrial Chemical Corp., Clairton, PA (1969), p 32

[4.8] VFT AG, Duisburg, Novares Techn. Info. 1. 1. 96 GB

[4.9] G. L. Brown, (see [4.7]), p 43

[4.10] G. L. Brown, (see [4.7]), p 41

[4.11] G. L. Brown, (see [4.7]), p 40

[4.12] J. P. Kennedy, E. Maréchal, (see [3.1]), pp 496–497

[4.13] D. O. Hummel, F. Scholl: Atlas der Polymer- und Kunststoffanalyse, 2. Auflage, Band 2, Carl Hanser Verlag, München, Wien; Verlag Chemie, Weinheim, Deerfield Beach, Florida, Basel, 1984

[4.14] Ullmann's Encyclopedia of Industrial Chemistry, Vol. A23, pp 94–96 (1992)

References for Chapter 5

[5.1] G. R. Hamed, C. H. Sieh, Rubber Chem. Techn. 58, p 1038 (1985)

[5.2] PSTC – Pressure Sensitive Council, 1201, Waukegan Road, Glenview, Illinois 60035, USA

[5.3] AFERA – Association des Fabricantes Européens de Ruban Auto-Adhésifs, 60, Rue Auber, F-94408 Vitry sur Seine Cedex (France)

[5.4] Shell Chemicals, Technical Bulletin TPE 5.2.1 (1995)
[5.5] Shell Chemicals, Technical Bulletin RBX/73/6
[5.6] Shell Chemicals, Technical Bulletin RBX/73/6
[5.7] J. B. Class, S. G. Chu, J. Appl. Polymer Sci. 38 (1985), 2, 805–842
[5.8] J. B. Class, S. G. Chu, Adhesive Chemistry, edited by Leing-Huang Lee, Plenum Publishing Corp., 1984, pp 269–296
[5.9] K. F. Foley, S. G. Chu, Adhesive Age, No. 9, 1986, pp 24–28
[5.10] J. B. Class, Rubber Chemistry and Technology, Vol. 58, 1985, pp 973–984
[5.11] J. D. Ferry, "Viscoelastic Properties of Polymers", John Wiley & Sons, Inc., New York, Chichester, Brisbane, Toronto, 1980
[5.12] K. F. Foley, Chu, (see [5.9])
[5.13] H. Kittel (†), Oberschwandorf (Germany): private communication
[5.14] Cray Valley (see [5.15])
[5.15] Cray Valley, Paris, Sartomer Company, Exton, Norsolene Hydrocarbon Resins for Paints and Varnishes
[5.16] W. R. K. Findley, "The Preservation of Timber", Black, London (1962)
[5.17] VFT AG, Duisburg, Novares Techn. Info. 1. 1. 96 GB
[5.18] Elf Atochem, Paris, Techn. Info. "poly bd", PBD 1002/01, 1004/01
[5.19] Nevcin Polymers B. V., Uithoorn, Techn. Data Sheet No. 233
[5.20] LRCC – Laboratoire de Recherche et de Contrôle du Caoutchouc, 60, rue Auber, 94408, Vitry sur Seine Cedex (France)

References for Chapter 7

[7.1] W. Edwar Deming, "Quality, Productivity, and Competitive Position", MIT Center for Advanced Engineering Study, Cambridge MA, 1982
[7.2] John S. Oakland, "Statistical Process Control, A Practical Guide", W. Heinemann Ltd., London, 1986
[7.3] R. A. Scouse, "Introduction to Statistical Quality Control", Plastics and Rubber International, Vol. 10, No. 1, pp 30-32 (1985)
[7.4] J. A. Cousans, S. H. Coulson, "Statistical Process Control – its role within the synthetic rubber industry", Plastics and Rubber International, Vol. 11, no. 4, pp 33-36 (1986)

References for Chapter 9

[9.1] Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 23, p 97 (1992)

Subject Index